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PRACTICAL RESULTS OF THE THEORETICAL DEVELOPMENT OF CHEMISTRY.*

BY

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COMMEMORATION days, festivals which revive the past and survey what has been done, are teachers of the future. The centenary of The Franklin Institute is truly a day worthy of celebration as a festival in all the branches of exact natural and applied science, for they have all been fostered and promoted by this Institute, and to it they owe much of their success.

Theoretical science in particular will unfold on such days of commemoration the impressive features of its development, and give a well-rounded picture of its progress, for in this sphere each conception is intimately linked to others. Individual domains are the more sharply defined, the deeper they are investigated; and all conclusions drawn and results obtained are brought together in the scientific literature of each special field of work.

In the sphere of applied science, the task is much more difficult. Here, not conceptions and theories as set down in writing are the landmarks, but deeds manifested in the reality of life. Writing describes the results, but rarely yields a complete picture of the course of a development, bringing a realization of its scientific, technical and economic premises and the difficulties of

* Address delivered Thursday, September 18, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

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each step in its progress. Nevertheless, it may even here be possible to outline to a limited extent a vivid picture of the development.

In the relations, however, of theoretical investigation to the development of its application to industry, we cannot proceed on these lines. The influence of the theoretical knowledge of one generation upon its application by the following is certainly of particular importance when viewed in the broad light of human culture. But this sphere of interrelations is so vast and the mutual influences of its elements so manifold, that one has to forego the attempt to give it an exhaustive presentation within the scope of one lecture, even in a single branch, as chemistry. Such a survey would be either a register of names and facts, or a kind of philosophical generalization. In both cases, the result would be without real interest for natural and applied science, the objects to which the work of The Franklin Institute has been devoted for one hundred years and toward which I am honored to contribute to-day as a testimony to this Institute.

May I therefore be permitted to limit my comment to but a few particularly notable points in the relations between theoretical and applied work in chemistry? Three of these have been my particular concern within the course of my studies: The development of dyestuff investigation in the epoch of structural chemistry, when I was a student of this science; the nitrogen problems in the first decade of this century, when the theory of thermodynamics was the pivotal point of experiment; and at present, in the epoch of atomic forces, the progressive development of capillary chemistry.

All the epochs in which the advancement of knowledge and the promotion of applied sciences are in intimate coöperation are marked by this one feature; their general conceptions are in harmony and the actual working methods are closely interrelated in research as well as in industrial laboratories. A most impressive example is the present state of affairs in electrophysics, and in this country a visit to the General Electric Company's plant in Schenectady will serve as the best illustration of what I mean. The state of affairs in the great organic chemical factories was similar forty years ago. At that period, the main task of theoretical science consisted in finding structural formulæ representing the synthetic experiments with simple carbon compounds,

and the applied science profited by every step forward, in the production from the same compounds of useful derivatives for the purposes of the dyestuff industries and of medicine.

Theoretical conceptions at that time were very simple. By chemical analysis the identity of the atoms constituting a molecule and their numerical ratio in it were found, while the determination of the molecular weight yielded the sum total of atoms present. The structural theory showed in which way the various atoms were grouped in the molecule, and the reactions were explained by the kinds, the number, and the arrangement of the atoms, without stating anything quantitative regarding their size, their distance from each other, and the physical forces acting between them. As a matter of fact, these simple data were sufficient to explain the main chemical characteristics of the carbon compounds in simple cases. These characteristics became manifest in the action of strong reagents and they were helpful in obtaining many products of great practical value, especially in the field of coal-tar constituents. Such a simple and non-physical conception, however, could not permit a further analysis of the subject. The structural pictures proved not at all distinct, nor were the valences constant. Differences in reaction were found by *experience* that would not fit into any structural picture. However, while the development of the structural theory met with considerable difficulties, its actual state, after the investigation of the simpler compounds, permitted a successful study of the more complicated natural products. The sugars, the tannin bodies, the alkaloids, the protein bodies and the vegetable dyestuffs were all exploited by organic chemistry.

But in the course of this development the direct relation between theoretical and applied work was weakened because the synthetic methods of obtaining the natural products could not compete in simplicity with the agricultural methods, except in a few cases, amongst which indigo is the most famous instance. An explanation lies in the fact that the synthetic methods are absolutely different from the natural processes in the formation of these substances.

For a short time a new field seemed to open for the coöperation of structural theory and preparative application, on the border-line of medicine and chemistry, giving the impression that the kind, the number and the grouping of the atoms in the

molecule would permit irrefutable conclusions concerning pharmacological action. There certainly exist here relations which by patience, combined in time with much experimentation, might be opened to practical utilization. But let us bear in mind that the living body is not at all homogeneous and that a relation insufficient even for safe deductions in the sphere of pure chemical reactions in a homogeneous system, could not therefore suffice for a satisfactory and unobjectionable explanation of the effects of pharmacological experiments upon the living organism.

Scientific organic chemistry of to-day considers its main object to be the investigation and copying of the natural processes in the formation of metabolic products, and this aim is widely different from that of applied chemistry in which, by organic synthesis, useful products are obtained from coal-tar and similar raw materials. The working coöperation of theoretical and industrial chemists has deteriorated into mere mutual instruction.

The great period of structural chemistry was followed in the final decade of the last century by an epoch which we might call the period of thermodynamics. The mere accumulation of facts in the sphere of inorganic chemistry had grown intolerable. A young generation welcomed enthusiastically the attempt to utilize thermodynamic knowledge, acquired by the previous generation, for the apprehension of facts in the sphere of inorganic chemistry. It was especially the theory of electrolytic dissociation and the application of thermodynamics to the *products of dissolution, the ions*, that threw light upon the domain of electrolytic processes just beginning to develop in practice. The new productive coöperation between theory and application was not, however, as intimate as had been that of organic chemistry in the former period. Thermodynamics by its nature only furnishes limits for chemical reactions, and defines the sphere of existence of chemical states, but it is on the whole unable to teach in which way within these limits reactions may satisfactorily be brought about. If compounds lend themselves easily to our experimentation, the practical chemist will have no difficulty in finding the proper conditions by tests, and while he will not underrate theoretical work, he will not consider it, in his own productive research, of primary importance. Indeed, in the physico-chemical period of which I am speaking, catalysis played the most important rôle for the productive chemist, while theory had to be content with stating

that catalyzers do not influence the equilibrium of chemical processes, and with determining the velocity of catalytic actions. Theory taught how to express, by differential equations, the time ratio for a given process. These equations, however, were of no avail in finding the catalyzers which facilitated the desired reactions.

In the special field of electrolysis some particular industrial methods were developed, among which the production of chlorine and alkali and the preparation of light metals hold the first place. Progress in this line was promoted by the instructive coöperation of theory. The general application of electrochemical methods was impeded by their restriction to processes of oxidation and reduction, as the nature of electrolysis limits its utility because of the sensitiveness of electrodes to impurities in the electrolytes and the difficulties connected with chemical actions in a plane. This limitation is in sharp contrast with the practical advantages of such actions in bulk for the construction of the apparatus and the arrangement of plants. Theory, however, came to a standstill in this application, just as it had been halted in general considerations because of the different reactions of electrochemical processes at chemically different electrodes.

At the beginning of this century, the nitrogen question brought up a problem in which the imperative need of coöperation in theory and practice became conspicuous. General concern was caused by the doubt whether, in the long run, agriculture could be supplied with the necessary quantities of fixed nitrogen by the vast fields of Chile, which were practically the only natural deposits. I remember my vivid impression, when visiting (for the first time) the United States in 1902, on seeing the first industrial experiment station to be established, that of the Atmospheric Products Company. The idea of copying the process of the combination of nitrogen and oxygen by lightning in the atmosphere, and in this way producing nitrogen oxides that could easily be transformed into nitric acid and nitrates, fascinated the world. In competition with this method, the process of the fixation of atmospheric nitrogen by calcium carbide was developing. Both these methods are to-day, however, of minor importance in agriculture in comparison with that of the production of ammonia from nitrogen and hydrogen.

At that time, the possibility of producing chemically even

traces of ammonia from its elements was disputed. Only the method of electrical production by silent discharge was proven. It is significant that the degree of stability of ammonia for the required synthesis was not even approximately known. Of course, the stability of the compound at ordinary temperatures seemed probable, in view of the amount of heat necessary for its formation. But after the numerous fruitless experiments of the previous generation, it seemed beyond doubt that nitrogen and hydrogen would not unite spontaneously at this temperature. Experiments at high temperatures, on the other hand, had up to that time proved nothing but its rate of decomposition, and alleged synthetic results turned out to be experimental errors, as the action of water upon nitrogen compounds or similar unintended by-reactions were answerable for the occurrence of ammonia. The first positive conclusion was the statement of the approximate ammonia content in mixtures (at 1000° C., by means of van't Hoff's rule of the shift of equilibrium by temperature) with nitrogen and hydrogen. This was proved by the reversible formation of traces of ammonia from these elements. This finding made it at once clear that there was no prospect whatever of producing the compound under ordinary pressure at temperatures from 500° C. upward. As, on the other hand, it was contrary to any experience that catalyzers of rapid action at lower temperatures might be found, synthesis at ordinary pressure had to be eliminated from the scope of preparative chemistry. But the same thermodynamic terms of van't Hoff furnished a quantitative expression of the extraordinary advantage of high pressure in this case for the determination of the position of the equilibrium, and the law of mass action clearly indicated the acceleration of the reaction by increasing pressure. Thus, in the beginning of the year 1905, a new possibility for the coöperation of the two forms of science was opened.

What thermodynamics can, and what it cannot give to synthetic chemistry, may be gathered from the significant fact that after these conclusions a pause of several years followed, during which the synthetic problems were not advanced, because nobody yet entertained hopes for their solution. Two further experimental steps were necessary, namely, the discovery of catalysts which would have a rapid action upon the nitrogen-hydrogen mixture under pressure at about 500°, and a device to bring about

by means of such catalysts the continual production and separation of ammonia under high pressure from a constant stream of the nitrogen-hydrogen mixture. The development of these two steps and the subsequent results accomplished by the Badische Anilin and Soda Works are widely known. The comparison of the present status of this branch of science with that revealed in the two reports published in the *Zeitschrift für Elektrochemie* for April, 1910, and January, 1913, may be left to others.

It might be deemed appropriate at this point to touch briefly upon the relations between the significance of ammonia synthesis under present conditions and the fixation of nitrogen by means of electrical discharge and by the help of calcium carbide. There are nowadays ammonia plants that obtain hydrogen by electrolysis and nitrogen from air, applying thus as raw material substances that are widely distributed and have a minimum economic value. We know that such plants yield a kilogram of nitrogen in the form of ammonia with approximately the same consumption of energy as is required for a similar effect in the cyanide industry, namely, about 17 kilowatt-hours. The cyanide industry, however, needs raw materials, such as coal and lime, that are not required in the production of ammonia. On the other hand, the production of nitric acid by means of the electric arc can be accomplished with the same raw material as that required in the production of ammonia; it consumes, however, three times as much electric energy.

The ammonia industry is a key industry and opens new paths to the production of nitric acid, of urea, and perhaps of hydrocyanic acid. Chemical industries, however, learning from one successful method how to solve other problems with the same means, are beginning to apply the high-pressure methods to other reactions of hydrogen, and in general to gas reactions in which the volume decreases. Consequently, the thermodynamic advantage of high pressure, which is of such decisive significance in ammonia synthesis, exists likewise in these other reactions.

The periods of structural chemistry and of thermodynamics in chemistry have been followed by a third period in which theory is beginning to interpret the structure of atoms by discrete electric constituents and the coherence of the atoms in the molecules by electric forces resultant from the action of the atomic constituents upon one another. The progress, during the last ten years,

in this theoretical field surpasses all expectations. But the new acquisition of knowledge is encumbered with a mortgage which complicates and retards its development, and makes every single step in the progress of the theory depend upon a new inspiration of genius. This mortgage is the impossibility of deriving the interrelation of the phenomena of motion of the electrically charged atomic constituents from the common laws of electrodynamics as well as from the theory of quanta. This latter theory has transformed all our ways of thinking in the sphere of atomic physics. Our most important auxiliaries, however, the fundamental conceptions of physics, continually prove unsatisfactory in the development of the theory. We always feel like a turner trying at his lathe to repair a watch. Under these circumstances, the connection between the interests of theory and of practical application to industry is nowadays limited in scope.

Among such common interests, however, there is one toward which development tends from all sides to such a degree that it is hard to tell whether it is of greater interest to the organic or the inorganic, to the experimental or the practical chemist. This bond is what we call capillary chemistry. The interest of the organic chemist is derived from his occupation with vital processes. He tries to make use of surface actions for isolating and purifying his preparations, as he works in a sphere where distillation and crystallization are no longer sufficient as auxiliaries. On a second ground, his interest is perhaps even deeper: The better he understands the chemical structure of the molecules in the substance occurring in living organisms, the more he is impeded by his ignorance regarding the relation between the chemical nature of the substances and the growth of the organisms. The powers of surfaces are apparently determined by the chemical properties of substances, and the morphological properties by the surface tensions. The most urgent and most important thing, however, equally interesting to the organic and to the inorganic chemist, is the relation of surface tension to the reactivity of foreign substances collecting at the surface of a phase. This is the problem of heterogeneous catalysis which is applied by nature in many of its most important vital processes and by chemistry in an exceedingly great number of reactions. And since, in industrial chemistry active carbon has become a daily

aid, the properties of adsorption become valuable for the production of the very volatile constituents of mineral oil, for the recovery of solvents, for the decolorizing of sugar juices, oils and fats, and, generally speaking, for all those cases in which a small, valuable, or disturbing constituent is to be separated from a mass of a gaseous or liquid phase. In these cases, however, industrial interests are far from exhausted. With colloids, such as leather, silk and wool, capillary chemistry is the exclusive scientific agency, whilst in the foodstuff industries, like those of milk and milk products, and in the industries of caoutchouc and artificial resins, or of clay, it is one of the principal foundations.

To these extensive and diverse applications of surface phenomena, there corresponds a multiplicity of theories, which are not fully linked together. Perhaps the following remarks will be welcome as a contribution to the relations of these theories.

The theory of adsorption owes its foundation to a conception of Gibbs, according to which the change of surface tension in a solution, with an increase of concentration, corresponds to a change of osmotic pressure in the solution with an increase of the surface. If the gas laws be valid for the dissolved substance, we have

$$RT\nu = -\left(\frac{d\sigma}{d\ln c}\right)_T \qquad (1)$$

In this equation of Gibbs, R is the gas constant, T the absolute temperature, ν the surface density of the dissolved substance at the adsorbing surface, c the molar concentration of the substance in the solution, and σ the specific free energy of the surface. The same equation is obtained when adsorption does not take place from a solution, but from a gas space in which the gas obeys the *Boyle Gay-Iussac Law*. In this case we have, instead of the concentration c, the gas pressure p. The application of this expression to the discussion of special problems is hampered by the fact that the surface density ν cannot be represented as a function of the concentration c or of the partial pressure p, and that consequently the isotherms of adsorption cannot be stated. Now v. Szyszkowski [1] has given an equation which he considers an absolutely valid empirical law and which indeed has often been successfully applied. He brings the free

[1] *Z. f. phys. Chem.*, **64**, 385 (1908). Freundlich, "Kapillarchemie," p. 86 (1923).

surface energy of the pure solvent σ_M and of the solution σ into relation with the concentration of the solution by two constants K and k as follows:

$$\sigma_M - \sigma = K\sigma_M ln\left(\frac{c}{k} + 1\right) \tag{2}$$

We differentiate and thus obtain:

$$-\frac{d\sigma}{dlnc} = K\sigma_M \frac{c}{c+k} \tag{3}$$

Comparison with (1) yields

$$RT\nu = K\sigma_M \frac{c}{c+k} \tag{4}$$

Let the isothermal constants R, T, K and σ_M be united into the symbol A, where $A = \frac{K\sigma_M}{RT}$. We obtain by elementary transformation

$$\frac{\nu}{A-\nu} = \frac{c}{k}. \tag{5}$$

This simple relation between concentration and surface density would be valid if the formula of v. Szyszkowski fully represented the facts. But experience teaches that the equation holds only approximately. Let us call this the "chemical" approximation and note that it expresses the essential content of Langmuir's equation, which is derived in a different way. For its interpretation, we may regard the adsorbing surface, for example that of an active carbon, as a structure with a definite maximum number of places that can be occupied by the molecules of the adsorptive. If all these places are occupied, the surface is saturated with the adsorptive. Denoting the maximum value of adsorption at unit surface of the adsorbent by $\nu_{max.}$ then $\nu_{max.} = A$ and $\nu_{max.} - \nu$ is clearly an expression signifying the vacant part of the surface, whilst ν signifies the occupied fraction.

Thus equation (5) passes over into:

$$k = c \cdot \frac{\text{vacant fraction of surface}}{\text{occupied fraction of surface}}. \tag{5a}$$

In this mode of expression, the equation denotes the equilibrium of a chemical reaction taking place according to the following scheme at the surface O:

$$x + O = xO$$

To make this plain, let us take as an example water vapor as the

adsorptive x, and a carbon surface as the adsorbent. We thus have the relation:

$$\text{Vapor of water} + \text{carbon} \rightleftarrows \text{hydrate of carbon.}$$

Here the first premise is that carbon and hydrate of carbon form one homogeneous phase, *i.e.*, a solution; and the second that the active masses of both may be represented by their mol fractions.

Of our two premises, the first one, which considers carbon and hydrate of carbon a homogeneous phase, is, as will be demonstrated, justified by thermodynamics. The second assumption, however, which substitutes mol fractions for the active masses, is surely too crude, and therefore only roughly approximates to the facts. The first premise states that water vapor is in no other relation to active carbon than it is to concentrated sulphuric acid, with which it reacts by forming a hydrate that mixes with the concentrated acid.

In any consideration of the phenomena of adsorption, it is a particularly important question whether the adsorption process produces an accumulation of the adsorbed substance only in the first, or in many of the molecular layers. Both these theories have been advocated. When in adsorption we have an accumulation of electrically neutral constituents of a gas or a solution with which to deal, it appears to be better to adopt the monomolecular view. For the action of any active substance upon a molecular layer of water separated from the surface by numerous similar layers, it is necessary to assume the presence of forces that permeate the neighboring water molecules and have a distant action. But the chemical forces, and the action of electric multipoles by which we nowadays try to represent chemical forces, diminish so rapidly with increasing distance, and permeate molecules of the same kind so incompletely that, beyond the neighboring molecules, only small residual actions remain. The essential part of the phenomena is expressed by the action upon the neighboring molecules. This does not mean that the surface density of the adsorptive changes by one leap into the normal volume density on passing from the first molecular layer to the next one. Nor do we assume that, for example, adsorbed water fully reaches the vapor pressure of pure water if one single molecular layer of it has condensed from a gas space on a carbon surface. But the conception really signifies that only an insignifi-

cant difference of vapor pressure is left, as compared with pure water, when the carbon surface is covered with one molecular layer of water molecules, and that the density of water at the distance of two molecular diameters is already similar to its density at infinite distance from the adsorbent surface.

Let us then call the solution consisting of the uppermost molecular layer of the adsorbent, *i.e.*, in our example, carbon, and the adjacent molecular layer of the adsorptive, *i.e.*, water, two-dimensional, since it has only the thickness of two molecular layers in the direction normal to the surface.

The chemical conception of the process of adsorption finds an analogy in the *homogeneous* mixture of two sulphuric acid hydrates, in equilibrium, with the water vapor above, and *not* in the *in-homogeneous* mixture of calcium oxide and calcium carbonate at the dissociation pressure of the latter. This follows already from the fact that the equilibrium pressure of the adsorbent substance varies along the adsorption isotherm.

How far the conception of solution is justified can be inferred from a consideration of the relation between Gibbs' formula and the expressions for the free energy of mixture of two liquids. Let us write Gibbs' formula as follows:

$$-\frac{d\sigma}{dv}\cdot\frac{dv}{dlnp}=RT_v \tag{6}$$

By simple transposition we obtain

$$-\frac{d\sigma}{dv}=RT\frac{dlnp}{dlnv} \tag{7}$$

Let us now consider what relation there is between the free energy of mixture of two liquids when the resulting mixture has one mol of the first (a with the vapor pressure p_a) and v mols of the second (b with the vapor pressure p_b). In this case the vapor pressure work terms A_a and A_b show the relation:

$$-\frac{dA_a}{dv}=v\frac{dA_b}{dv} \tag{8}$$

The differential quotients are in the sense of Helmholtz those forces that bind the one or the other constituent of the binary solution in it. If we, however, express the vapor pressure work terms A_a and A_b by help of the gas laws, we obtain:

$$-RT\frac{dlnp_a}{dv}=RT\frac{dlnp_b}{dlnv} \tag{9}$$

and this is nothing but the well-known formula of Duhem and Margules. Thus the change of vapor pressure work for a is inversely equal to the change of vapor pressure work for the other constituent b for an isothermal change of the mixing proportion. The similarity between equations (7) and (9) is conspicuous. Indeed, formula (7) follows immediately from the analogous consideration of the isothermal distillation of ν mols of a liquid to the unit surface of an adsorbent, if we bear in mind that the specific free energy of the adsorbent surface sinks in proportion to the progressing distillation, and that the progressive load by distillation can be reversed by a thermodynamic machine pressing liquid water out of the two-dimensional solution, and thus increasing the specific free surface energy of the adsorbent. The relation between equations (7) and (9) will appear even more intimate when we measure $d\sigma$ directly by the change of the vapor pressure work, $RTdlnp_a$. It is irrelevant in our case that the vapor pressure p_a of carbon escapes determination. It is much more important that we can conceive this experiment, at all events theoretically, even if the adsorbent has a thickness of only one molecular layer. To demonstrate this, let us imagine that we evaporate a thick mass of the adsorbent charged with adsorptive, proceeding in such a manner that the vapor of the adsorbent is permanently removed by means of semi-permeable walls. The two-dimensional solution is not changed, neither in extension nor in its composition. The effect simply consists in the evaporation of the lower layers of the solid adsorbent.

Owing to the close relation obtained between the thermodynamic properties of the solution and the adsorptive layers, the same approximations are valid for adsorption and for solutions. For dilute solutions, the approximations are the well-known limiting laws of vapor-pressure depression of the solvent, with increasing concentration of the dissolved substance. But with regard to concentrated solutions Dolezalek [2] has shown that within certain limits the equation holds good:

$$\frac{dlnp_b}{dln\nu} = a$$

where a is a constant considerably larger than 1. Let us call this approximation the "physical" one. It was successfully applied

[2] *Verhandl. d. deutschen physikal. Gesellschaft*, 1903.

by Dolezalek for the purpose of expressing the electromotive forces of galvanic cells as a function of the salt content of concentrated electrolytic solutions. Exactly the same approximation was introduced by H. Freundlich as the adsorption isotherm. While its sphere of application for gas adsorption is but limited, it has been confirmed by experience in the adsorption of solutions to such an extent that, in spite of its empirical character, it has been applied almost as the fundamental law of these phenomena in the entire literature of the field. One can see at once that the introduction of this approximation between the specific free surface energy and the surface density in the isotherm gives:

$$\sigma_{\nu_1} - \sigma_{\nu_{11}} = RT(\nu_{11} - \nu_1).$$

From these considerations a simple transition is found to the electrocapillary and electrokinetic phenomena, by transforming equation (8) into:

$$-\frac{dA_a}{dA_b} = \nu. \tag{10}$$

In comparing this with Gibbs' formula in the form

$$-\frac{d\sigma}{RTdlnc} = \nu \tag{10a}$$

we recognize at once that

$$dA_a = d\sigma$$

$$dA_b = RTdlnc$$

Since, however, $RTdlnc$ is nothing but the change of the electrical force with the concentration of an ion determining the potential difference between two phases, we may substitute for $RTdlnc$ this change of potential difference dE [3] and thus obtain the Lippmann-Helmholtz formula of electrocapillarity, in which ν now denotes the excess of ions of one sign over the ions of the other sign on the unit surface of the adsorbent.

Charged constituents do not behave quite in the same way as uncharged constituents in the process of adsorption at a surface. Helmholtz, knowing of no ions, assumed that the charge formed a double layer of electricity, infinitely near on both sides to the border plane of the two phases. The solid body possessed in its

[3] Professor Otto Stern in a conversation about this point has told me that Professor Vollmer has come to the same conclusion, which he seems not to have published.

entire mass the same potential, as did also the liquid, and at the common surface the value of the potential sprang from one value to the other. This conception had to undergo a change as soon as the ions were recognized as the bearers of the charge in the liquid and their heat motion, or, in other words, their osmotic pressure, was taken account of. In order to obtain a clear conception, let us conceive the formation of a potential difference between the two phases, one solid and the other liquid, in accordance with Nernst, as a process in which some ions pass from the one phase to the other, so that in the liquid one kind of ion is somewhat in excess of the other. This excess furnishes the thermodynamic potential difference. The excess ions of one kind are not, according to Billiter and Gouy, accumulated in the last monomolecular layer of the common surface, but are disseminated into the depth of the electrolyte. Their density decreases, as shown by Gouy, according to an exponential function, with increasing distance from the surface. The grade of the exponential curve, that is to say, the exponent, grows in proportion to the increasing concentration of the ions in the solution. The shift of the excess ions of one kind into a greater depth is due to the fact that the charge located on the surface of the solid acts on monopoles even at a considerable distance. Thus, the osmotic pressure striving for equal distribution of the ions is counteracted by the electric force, not only at molecular distances from the surface, as in the case of neutral substances, but with decreasing intensity also in more distant layers. The excess of ions of one kind over those of the other, distributed in depth, brings about a gradient of potential in the liquid. So far as such a gradient exists still in layers of liquid which are conveyed by its motion and which change their position relatively to the immobile particles, it becomes manifest in electrokinetic experiments and brings about the electric phenomena known as cataphoresis and as electrokinetic potentials. This theory of Gouy forms a supplement to the well-known theory of the thermodynamic difference of potential between two phases. Generally speaking, the addition of salts to the solution may produce chemical changes of the solids in contact with the solution, thus modifying the thermodynamic potential difference. But this addition is no less able to change the distribution of the excess ions of one kind at constant thermodynamic potential difference.

The theory of Gouy does not fully account for the actual

values of the polarization capacity. Further, there is no explanation for the change of sign of the electrokinetic potential, found by Freundlich and Rona in some cases, in which the thermodynamic potential difference remained the same. This deficiency has lately been overcome, as it seems, by Otto Stern, who discussed this question at this year's meeting of the Deutsche Bunsen-Gesellschaft.[4] His assumption is that adsorption produces a monomolecular layer of ions along the adsorbent surface. Whether the ions of one kind or of the other are in excess in this layer depends upon their adsorption properties. The excess charge disseminates itself into the depth of the electrolyte, in harmony with the considerations of Gouy. The sign of the ionic cloud extending into the interior of the electrolyte, with an exponentially decreasing density, is that of the excess ions present in the first molecular layer. This excess may have either sign, owing to the action of adsorptive forces, and yet the thermodynamic potential difference between the solid body and a remote layer inside of the solution need not change. Otto Stern does not discuss the nature of the adsorptive forces. There is, however, no difficulty in assuming a particular action of the surface on the properties of the ions, and especially on their unequal distortion through the atom fields, to the significance of which attention was drawn formerly[5] in the related case of heterogeneous catalysis. These relations open the door to an understanding of coagulation phenomena, some of which are of special importance for biological processes. We will restrict our discussion to those which do not lend themselves to a simple chemical explanation.

The analysis of the ionic distribution in a conducting fluid surrounding one single solid particle yields the electrokinetic potential. The interaction of many such particles, with their ionic clouds between each other, seems to be the cause of coagulation. The older considerations indicate that as the ionic clouds all possess the same charge, they repel each other, while the discharged particles coagulate at the isoelectric point. This older conception does not coincide well with experience. Coagulation does not occur with high values of the electrokinetic potential, but it does take place, as Powis has shown under Donnan's direction,

[4] The paper has not yet been published. Compare Freundlich's "Kapillarchemie," third edition, page 342, where curve 2 gives the fundamental idea.

[5] See author's Nobel Lecture.

when the potential still differs distinctly from zero. The older conception is at the same time difficult to understand, because it involves a new type of action at a distance, for the particles of a gold sol anchor together, as Smoluchowsky's calculation of Zsigmondy's measurements has shown, even if their distances far exceed a molecular diameter. Never could metallic vapors or similar neutral gases form crystals by cooling if neutral particles, consisting of a charged nucleus and an oppositely charged envelope, were always kept apart by the repulsion of those envelopes. The ionic clouds around the colloidal particles are by no means rigid and their tails, especially, are easily displaced. Mechanically speaking, these clouds undergo definite formations; in electrical terms, they become polarizable. Coagulation means the formation of regular groups of particles held together through the intermediate charges of the enveloping ionic clouds. The closer these particles, consisting generally of substances heavier than water, arrange themselves together into structures of crystal character, the more the ionic clouds crowd to them; and the closer the structures are grouped, and the more their density therefore exceeds that of the electrolyte, the easier it is for them to form a deposit. But this formation of a deposit, which we call flocculation, is only a limiting phenomenon. In concentrated colloidal solutions, as Szegvary[6] has shown experimentally, the electric forces, properly adapted to the average distance of neighboring particles by addition of certain amounts of salts, will build up a perfectly regular system of particles, the formation of which gives rise to a semi-rigid state of the whole fluid. This pseudo-solid state is easily destroyed by shaking, and it reconstructs itself afterward in a definite time. These regular arrangements, which form most easily if the particles are not spherical, produce a kind of elastic resistance, discovered by Freundlich and his co-workers, even if they are not kept together by electric forces strong enough to produce distinct rigidity of the liquid. The most interesting case I know of was discovered by Locher with a liquid iron sol, the particles of which always arranged themselves in consecutive layers of about half a wave-length of green light.

Debye and Hückel have associated the laws of dilute electrolytic solutions with the behavior of charged particles. The preceding consideration may perhaps call the attention of mathe-

[6] *Kolloid Zeitschr.*, 1923.

matical physicists to the fact that there is another connection between the behavior of these particles and the usual crystallization phenomena.[7]

Let us review our theoretical discussions.

We have shown the intimate relation of Gibbs' formula to the thermodynamic theory of the free energy of mixture, permitting us to regard the adsorbed layer upon the surface of the adsorbent as a solution of both these substances in each other. Considering this solution from the chemical standpoint, we have found a simple explanation for Szyszkowski's empirical law, while, as a physical approximation, we could explain Freundlich's expression for the adsorption isotherm.

Langmuir's view of the monomolecular character of the adsorption layer we accepted for the class of uncharged substances as a consequence of the rapid fall of chemical forces with increasing distance.

Gouy's views, further developed by Otto Stern, gave us the understanding of how the electrokinetic potential could be of opposite sign to that of the thermodynamic. Applying those considerations which concern osmotic and electric forces to the case of many charged particles in the same liquid, we could enter the domain of the phenomena of coagulation, including flocculation, of the peculiarities of the resistance and of the rigidity of colloidal solutions. These phenomena seem to bridge the great gulf which separates crystals from solutions and are akin in many respects to Lehmann's liquid crystals.

We look back now to the past in order to learn for the future, and to-day we stand here in the shadow of Benjamin Franklin, whose name is written with indelible letters in the history of mankind as a physicist and as a statesman in the history of two continents. We may well ask therefore what these developments, of which we have only picked out a few, have meant to mankind. Nothing that man creates, either in pure or applied science, is of value for its own sake. Its advantage to mankind is the measure of its value.

[7] As a first approximation we may consider the semi-rigid or flocculated system of particles and ionic clouds as a heteropolar crystal, the ions of one sign being represented by the particles together with the main part of the clouds, the ions of the other sign being represented by the tails of the ionic clouds, while the distances are derived from the formula of Gouy or of Debye and Hückel.

Within the thirty years previous to the World War, we enjoyed all the precious gifts that were given us by the power of advancing knowledge. The state of science enabled industry to produce a thousand new commodities of life, and the economic world welcomed any successful attempt to offer them to mankind. But, alas, life is not eternal, and the reverse of the medal is visible to-day. The new commodities of life have become necessities. Industry has educated man to needs that were formerly unknown and has aroused in every one demands that must be granted for the sake of social peace. How can these demands be satisfied? There are two answers to this question. The one which is most adhered to in this country is that we should aim at a greater and cheaper production by increasing the utilization of natural resources. The other view, advanced as a new creed with the enthusiasm of a world conqueror, comes from Russia. It strives to attain success by disregarding personal competition and controlling production by the State. Neither of these ways will lead to the goal. The progressive education to new needs outweighs the progressive increase of production, while the elimination of free competition paralyzes the natural powers of man. To arrive at the goal we must have recourse to the primary origin of the difficulty. We produce goods as far as we know how to produce them, by virtue of our scientific and technical knowledge. But we are not able to produce those goods that we need most urgently. Nowhere else can we realize this malproportion more than in the sphere of chemistry, because, outside of chemistry, industrial efficiency is always restricted by the suitability of the material used, and because every transformation of the material belongs to the domain of chemistry. The most urgent chemical work, which we ought to but hitherto could not do effectively, is the providing for our sustenance and our health. Nutrition and cure are the tasks of natural science which open new fields to industry and new prospects of a happier state for man. We are scientifically far enough advanced in our knowledge of the minute difference between the structure of starch and that of cellulose. But we are not far enough advanced to be able to live on the stalk instead of the grain of wheat. To the first of the three periods of the above-mentioned coöperation between theoretical and applied science, we owe the discovery that nature can be surpassed. Our dyestuff industries offer a greater variety and

far superior quality of products. To the same period, we owe certain remedies which combat devastating maladies and alleviate pain that formerly tormented man severely. To the second period of coöperation, we are indebted for a progressive development in the providing of agriculture with the indispensable vegetable nutriments. Of the third period, in which we are living, we expect the exploration of those paths on which nature brings forth her living products.

There was a past when scientific development was not limited by time. What one generation did not discover was left to the next generation. The social condition of the world was not dependent upon scientific progress. To-day we are under some compulsion. Discontent with economic conditions arouses a strife amongst men, and only the progress of natural science offers the certain prospect of a greater contentment than prevails in the present world. This progress of natural science, however, can only follow from research work in the institutions of all civilized countries and from the coöperation of the politically distinct nations in this field of common interests.

Oscillations of Water in Turbine Installations. H. BUSCH. (*Physik. Zeit.*, Jan. 1, 1925.)—When water is taken from a reservoir through a pipe to the turbine, it is common to join to the pipe close to the turbine a vertical stand-pipe, so that a sudden shutting off of the flow through the turbine may not be followed by dangerous increases of pressure in the system. The contents of reservoir, penstock and stand-pipe together constitute a system capable of oscillation, which may die down or, unfortunately, may grow in size. In the latter case difficulties in operation will occur. It has been found that the growth of the oscillations is due to the apparatus regulating the turbine, which keeps constant the output of energy. Since this is proportional to the product of the water passing through the turbine in unit of time by the difference of level from stand-pipe to tail-race, it is seen that these two quantities vary inversely, the quantity of water discharged increasing as the difference of level decreases. From this peculiar relation Thoma has shown the growth of oscillations to arise in those cases in which the damping due to frictional resistance to the flow of the water is not too great. The author describes a simple apparatus to demonstrate the growth of oscillations. A mechanical valve is arranged so that as the pressure at the discharge tube increases the flow of water is diminished, in imitation of the conditions at the turbine. The action somewhat resembles that of a hydraulic ram. It may serve further as a mechanical model of the vibrating arc of Duddell and Poulsen. G. F. S.

THE INFLUENCE OF J. WILLARD GIBBS ON THE SCIENCE OF PHYSICAL CHEMISTRY.*

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IT HAS often happened in the history of science that after or during a period of activity, there has come a man of genius, who, combining profound insight with the highest powers of logical reasoning, has presented the world with a precisely formulated and far-reaching synthesis of scientific principles. We see the first great physical synthesis of this sort in the laws of motion and the theory of universal gravitation as enunciated by Newton in the seventeenth century. The further study of the laws relating to the motion and equilibrium of material bodies culminated in the great and comprehensive formulation due to Lagrange and Hamilton in the eighteenth and early nineteenth centuries.

When we endeavor to trace the history of thermodynamics, we find a similar development; the great step taken by Carnot, the gradual recognition of the general principle of the conservation of energy, the statement of the second law by Clausius and Kelvin, and finally the great, comprehensive, and generalized statement of Willard Gibbs, whose work bears the same relation to the science of thermodynamics that the work of Lagrange and Hamilton bears to the science of mechanics. The wonderful power of profound reasoning and extreme generalization possessed by Gibbs entitles him to an equal rank in an allied branch of science. Clerk Maxwell and Boltzmann, perceiving that in the development of the dynamical theory of gases, the principles of mechanics must be supplemented by statistical reasoning, had established the very important science of statistical mechanics. Their investigations applied to a system containing a vast assemblage of molecules in random motion. Gibbs, not content with his generalized analytical and geometrical formulation of thermodynamics as based on the "empirical" principle of entropy, and seeking a rational foundation for this branch of science, turned his attention to statistical mechanics. In charac-

* Address delivered Friday, September 19, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

teristic manner, he proceeded to apply dynamical and statistical reasoning not merely to a single assemblage of molecules but to a vast, though unconnected, assemblage or "ensemble" of systems subject to the same dynamical laws and each characterized by a very great number of degrees of freedom. Not only did he obtain the rational foundation of thermodynamics which he sought, but the science of statistical mechanics received an extension and generalization comparable with that given by Lagrange and Hamilton to the science of mechanics.

Writing some fifteen years ago, Henry Adams stated that, after Benjamin Franklin, Gibbs was the greatest man of science America had produced. He might well have added that in the history of the physical science of the seventeenth, eighteenth and nineteenth centuries, Gibbs ranks with men like Newton, Lagrange, and Hamilton, who by the sheer force and power of their minds have produced those generalized statements of scientific law which mark epochs in the advance of exact knowledge.

In the first two papers published by Gibbs, he made great advances in the application of geometrical methods to the study of the thermodynamic properties of substances. We may say, indeed, that already in these first two papers, he created the *general* subject of graphical thermodynamics. The new geometrical methods developed by Gibbs have been of the utmost importance to the scientific engineer, who was thus provided with a tool comparable in power and scope with his graphical statics derived from the science of mechanics. The discussion of the volume-entropy-energy surface contained in the second paper, which attracted the attention and admiration of Maxwell, opened up a new, powerful and fertile field in physico-chemical science. We see here the great herald and precursor of that long series of triumphs which Gibbs' methods were destined to achieve in later years.

About two years after the publication of this paper, there began to appear in the *Transactions* of the same learned Society (the Connecticut Academy) one of the mightiest works of genius the human mind has ever produced, namely, the memoir "On the Equilibrium of Heterogeneous Substances." For this was nothing less than the creation of a complete and perfectly general thermodynamical theory of physico-chemical equilibrium. At the time when Gibbs wrote this paper, very little was known about the physical nature of atoms and molecules, except their relative

masses. He saw, however, that a great advance was possible by an extension and generalization of the fundamental principles of thermodynamics, since these can be stated without reference to atomic and molecular magnitudes. As we know from his writings, Gibbs was certainly no disbeliever in, or despiser of, the atomic and molecular concepts. Realizing, however, the meagreness and uncertainty of this knowledge, he determined wisely to build on a sure foundation, and he saw that this foundation was provided by the theory of energy and entropy. The result was the creation of an almost entirely new physico-chemical science, which we may, for want of a better word, call thermodynamic chemistry.

Since 1900 the rapid advance of modern physics has supplied chemical science with many powerful weapons in the shape of new ideas, new facts, and new experimental methods. Modern knowledge concerning the physical nature of the electron, ion, atom and molecule, has, indeed, created a new science in which nearly all the artificial distinctions between physics and chemistry have vanished. In the period 1878–1900, Gibbs effected a similar fusion, by uniting physics and chemistry in a great science of equilibrium, in which the statistical equilibria of masses of matter, enormously great in comparison with molecular magnitudes, were deduced from the two laws of thermodynamics in the most complete and general manner.

This creation by Gibbs of a comprehensive physico-chemical thermodynamics was, and long will be, of enormous importance both for chemistry and physics. However much we may learn about the individual units of the physico-chemical world, we shall always be vitally concerned with certain very important aspects of the average behavior of the "crowd." Perhaps in time statistical mechanics or statistical electromagnetics will supply all the knowledge we require, but these branches of science have still a long way to travel before that goal is reached. Even in very recent years, the "electron crowd" has come under the sway of thermodynamical methods, as, for example, in the case of thermal ionization and other types of electron emission and absorption.

Many have been the impulses which have helped to carry chemistry forward toward the goal of an exact science, such as, for example, the recognition of the elements and their conservation, and the atomic and molecular theories. With the names of

Boyle, Black, Lavoisier, Dalton, Avogadro, and Cannizzaro, we must surely also associate the name of Gibbs, for from his work came one of the mightiest of the impulses which have rationalized chemical science.

The generalized system of thermodynamics created by Gibbs was so extensive and detailed that on an occasion such as the present, it would be impossible to give even the most inadequate outline. Such an attempt is rendered all the more unnecessary since a number of able physicists have expounded its main principles. It would be impossible, however, to do even the barest justice to the subject of the present article without saying something about the fundamental ideas which Gibbs introduced into this branch of science.

Applied to a homogeneous system characterized by a uniform temperature t and a uniform pressure p, and subject to no other external forces except that due to this pressure, the development of thermodynamics up to the date of Gibbs' researches may perhaps be briefly summarized in the equation of Clausius, $\delta u = t\delta s - p\delta v$, where u = energy, s = entropy, and v = volume. This equation applies to a closed system of *constant* total mass, and the first fundamental step taken by Gibbs was to extend it to a system of *variable* mass. In the equation of Clausius the entropy of the system may be changed by the addition or subtraction of heat, whilst the volume may be altered by work done by or on the system, both types of change producing corresponding changes in the energy. It is possible, however, simultaneously to increase or diminish the energy, entropy, and volume of the system by increasing or diminishing its mass, whilst its internal physical state, as determined by its temperature and pressure, remains the same. If we are dealing with a system whose energy, entropy and volume may be regarded as sensibly proportional, at constant temperature and pressure, to its mass, we may write:

$$du = \delta u + u_o dm$$
$$ds = \delta s + s_o dm$$
$$dv = \delta v + v_o dm$$

where the total differentials du, ds, and dv indicate changes which take account of variation of mass at constant temperature and pressure as well as of heat and work effects at constant mass

(indicated by the differentials δu, δs, δv) and u_o, s_o, v_o denote the energy, entropy, and volume, respectively, of unit mass under the specified conditions of temperature and pressure. Combining these equations with that of Clausius, we obtain

$$du = tds - pdv + (u_o - ts_o + pv_o)\,dm$$

or, putting

$$u_o - ts_o + pv_o = \mu$$

$$du = tds - pdv + \mu dm.$$

Gibbs called μ the *potential* of the substance constituting the system. The great significance and generality of Gibbs' method lay in the fact that he started with the extension of this equation to a homogeneous mass of matter or *phase* containing any number of independently variable components, *i.e.*,

$$du = tds - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \text{etc.},$$

where m_1, m_2, etc., denote the masses and μ_1, μ_2, etc., the corresponding potentials of these components of the phase. This famous equation is the starting point of Gibbs' investigations. Its great importance lies in the fact that it takes explicit account of variations of the composition and mass of the phase, so that it becomes possible to deal with the mutual interactions and equilibrium of coexistent phases of matter, that is to say, with *heterogeneous* systems. The first important result was that the distribution of any component throughout any series of coexistent phases in equilibrium is determined by the equality of the potential of this component in the various phases. It was thus evident that in the theory of physical equilibrium the potential of a component plays a rôle analogous to that of temperature with regard to heat. Another result of the greatest importance was the deduction of the famous "phase-law," expressed by the equation

$$v = n + 2 - r$$

where v = the number of independent variations compatible with the coexistence of the phase complex, or internal thermodynamic degrees of freedom of the system, r = the number of coexistent phases in equilibrium, and n = the number of independently variable components. Perhaps in the whole history of science no other linear equation of equal simplicity has had a wider significance and influence. One may truly say that it has been a veritable pole star in the exploration of vast domains of modern chemistry.

As Gibbs showed, his initial equation can be expressed in several different forms which are of great service in the investigation of states of equilibrium. If, for example, the temperature and volume remain constant,

$$d(u - ts) = \Sigma \mu dm$$

which may be briefly written in the form

$$(dA)_{v,t} = \Sigma \mu dm$$

where (following the nomenclature of G. N. Lewis and A. A. Noyes) we denote the quantity $(u - ts)$ by the symbol A. Thus any potential μ_k may be defined by the equation

$$\mu_k = \left(\frac{\partial A}{\partial m_k}\right)_{v,t,m}$$

where the subscript m denotes that all the other masses save m_k remain constant in the differentiation. The function A possesses particular importance with regard to the maximum capacity of a system to perform external work in passing from any one to any other of a series of *monothermic* states, *i.e.*, states characterized by the same value of the temperature. Denoting the initial and final states by the subscripts 1 and 2, respectively, then, if we bring the system by a reversible process from state 1 to state 2:

$$A_1 = u_1 - ts_1, \quad A_2 = u_2 - ts_2$$

so that

$$A_1 - A_2 = (u_1 - u_2) + t(s_2 - s_1) = -\Delta u + Q = W$$

where Q and W denote, respectively, the heat taken in and the work done by the system in the reversible process. The decrease of A is therefore equal to the maximum work which the system can yield in the specified monothermic change. The function A, called by Helmholtz the *free energy*, occupied a prominent position in his thermodynamical investigations, though nothing essentially new was added to the results obtained by Gibbs.

For changes at constant temperature and pressure, it follows from Gibbs' fundamental equation that $d(u - ts + pv) = \Sigma \mu dm$. If we denote the quantity $(u - ts + pv)$ by the symbol F (again following the nomenclature of Noyes and Lewis), the above equation may be written in the form

$$(dF)_{p,t} = \Sigma \mu dm.$$

We may thus define any potential μ_k by the equation

$$\mu_k = \left(\frac{\partial F}{\partial m_k}\right)_{p,t,m}$$

By integrating with respect to mass at constant temperature, pressure and composition, we arrive at the result

$$F = \Sigma \mu m.$$

The potentials in a multi-component phase thus appear as the mass coefficients in the expression for F. If we follow Noyes and Lewis and call F the free energy, we may therefore call the potentials the "partial free energies" per unit of mass of the several components.

Gibbs showed that the general conditions of equilibrium could be expressed in either of the variational forms

$$(\delta A)_t \geqq 0, \quad (\delta F)_{p,t} \geqq 0.$$

For systems capable only of bilateral variations (*i.e.*, systems such that to every variation of A or F there corresponds an equal and opposite one) these conditions reduce to the equations

$$(\delta A)_t = 0, \quad (\delta F)_{p,t} = 0.$$

The value of Gibbs' concept of the potential, however great it was in dealing with physical interaction and equilibrium in heterogeneous systems, was even more strikingly exhibited by his investigation of chemical equilibrium in a single phase. For the first time in this history of science, the method of Gibbs enabled the equation of chemical equilibrium in a homogeneous system to be expressed in an exact and yet perfectly general form, since, for internal equilibrium in a homogeneous mass, $\Sigma \mu dm = 0$. If the components in such a closed phase are all independently variable, this equation is devoid of meaning. But if reversible chemical reactions are possible among these components or among some of them, so that a group of components cease in this manner to be independently variable and become mutually convertible, the equation $\Sigma \mu dm = 0$ applied to this correlated group supplies a restrictive condition which reduces the number of independently variable components. Thus, suppose we have a phase containing three components, X_1, X_2, and X_3, amongst which a definite reversible chemical reaction occurs, for example, such that X_1 and X_2 react to give a compound X_3. For equilibrium

$$\mu_1 dm_1 + \mu_2 dm_2 + \mu_3 dm_3 = 0,$$

whilst the chemical mass relationships yield the equations

$$-\frac{dm_1}{a_1} = -\frac{dm_2}{a_2} = \frac{dm_3}{a_3}$$

where a_1, a_2 and a_3 are positive quantities. It follows that for chemical equilibrium

$$a_1\mu_1 + a_2\mu_2 = a_3\mu_3.$$

This equation amongst the chemical potentials expresses in the present case the finite and perfectly general equation of chemical equilibrium obtained by Gibbs.

However important these results were in their great generality, they would have remained at first comparatively barren had it not been that Gibbs was able to obtain expressions for the potentials in two important cases, namely, in the case of ideal gas mixtures and in the case of dilute solutions. The result in the case of gases enabled him to test and verify his equations by means of known experimental data. This establishment of the equation of chemical equilibrium for a mixture of gases in a practically useful form was of the greatest possible importance for the development of chemistry, though perhaps few chemists were able to understand or use it until van't Hoff arrived at the same result by means of the maximum work principle as applied to his famous "equilibrium box" with its pistons and semi-permeable membranes.

Of no less importance was Gibbs' remarkable demonstration that in the case of a component occurring in very small concentration in any homogeneous mass, the potential could be expressed by the approximate equation, $\mu = At \log c + k$, where c is the concentration of the component, A a constant characteristic of the component, and k a function of the temperature as well as of the nature of solute and solvent. It transpired later from the work of van't Hoff on dilute solutions that if μ and c be referred to the Avogadrian molar mass of the solute, A becomes identical in the limit with the universal gas constant R.

The whole thermodynamical theory of dilute solutions, including the law of chemical equilibrium, flows from this result, so that Gibbs must be regarded as the essential founder of this theory, though it remained for van't Hoff and others to rediscover and apply many of his results.

We may trace the influence of the Gibbs-van't Hoff equation,

$\mu = RT \log c + k$, in an important modern formulation of the thermodynamics of solutions initiated by G. N. Lewis and extended and developed chiefly by him and by J. N. Brönsted. The potential μ may be regarded as a measure of the tendency or potency of a substance to escape from a phase. It was, no doubt, a recognition of this fact that caused Gibbs to employ the term "potential." Now we may *define* a quantity f (fugacity) by means of the equation

$$\mu = RT \log f + k$$

where, for any given substance k is a function of temperature, but not of concentration, and employ f instead of μ as a measure of the "escaping tendency" of a component of a homogeneous mass or phase. Such a procedure has the practical advantage that, as the concentration diminishes, f approaches zero, whilst μ tends toward the value $-\infty$. Another advantage lies in the fact that by using f we can express the thermodynamic relations for solutions or phases of any degree of concentration in exactly the same mathematical form in which these relations are expressed for very dilute solutions, since in the latter case f tends toward the value of c. Thus, in the previously quoted case of chemical equilibrium, the equation of Gibbs

$$a_1\mu_1 + a_2\mu_2 = a_3\mu_3$$

(where, if we refer the μ's to molar quantities, the a's represent small integers) becomes

$$\operatorname{Log} \frac{f_1^{a_1} \cdot f_2^{a_2}}{f_3^{a_3}} = \frac{a_3k_3 - a_1k_1 - a_2k_2}{Rt}$$

The law of chemical equilibrium at constant temperature may therefore be expressed in the quite general form

$$f_1^{a_1} \cdot f_2^{a_2} = Kf_3^{a_3},$$

where K is a function of temperature, whilst as the solution becomes more and more dilute, this equation tends more and more closely to coincide with the form

$$c_1^{a_1} \cdot c_2^{a_2} = Kc_3^{a_3}.$$

Furthermore, the ratio $\frac{f}{c}$ for any given component is a measure of its deviation under any specified conditions from the law of

"ideal solutions." It is thus possible to connect some of the most recent thermodynamical formulations with the investigations and results of Gibbs. It is a great pity that many cultivators of the science of thermodynamics since the time of Gibbs have not gone back to the fountain head and closely correlated their results with his. Thermodynamics is a science whose principles and methods have been rewritten a great many times, often to the confusion, or at all events, the perplexity of the student and investigator. If certain writers on this subject since the time of Gibbs had made it their business to expound, and if necessary to explain and develop, his methods, it is very probable that progress would have been more rapid and that in certain cases much confusion would have been avoided. In this connection it is only fair to say that the greatest credit attaches to the efforts made by Wilder D. Bancroft (in the earlier volumes of his *Journal of Physical Chemistry*) to have the methods and results of his great fellow countryman explained to a rather ignorant scientific public. As an illustration of these remarks, we may consider the operation of reversibly transferring a component from a pure system to a solution (liquid or gas) system, an ideal process which has played a leading rôle in many expositions of thermodynamic chemistry. Let us denote the pure component system by the subscript *o* and the solution system by the subscript *s*. The reversible transference may take place either at constant volume and temperature or at constant pressure and temperature. In the former case, the volumes, in the latter the pressures of both systems remain constant.

1. CONSTANT VOLUMES AND TEMPERATURES.

Denoting the maximum work obtainable in the infinitesimal isothermal transference by $W_m dm$

$$W_m dm = -dA = dA_o - dA_s$$

Hence, per unit mass of component k transferred to an infinite solution system,

$$W_m = \left(\frac{\partial A_o}{\partial m}\right)_{v,t} - \left(\frac{\partial A_s}{\partial m_k}\right)_{v,t,m}$$

$$= (\mu_k)_o - (\mu_k)_s$$

2. CONSTANT PRESSURES AND TEMPERATURES.

In this case, also, as we are dealing with an isothermal change,

$$W_m dm = dA_o - dA_s.$$

In general $F - A = pv$ and therefore at constant pressure $dF = dA + pdv$. Hence we have

$$W_m dm = dF_o - dF_s + [(pdv)_s - (pdv)_o].$$

Now the terms inside the bracket on the right-hand side of this equation refer to work effects due to the volume changes of the two systems. When, as will often be the case, these work effects are not reckoned, or do not count as useful external work, we have, per unit mass transferred to an infinite solution system,

$$W_m = \left(\frac{\partial F_o}{\partial m}\right)_{p,\,t} - \left(\frac{\partial F_s}{\partial m_k}\right)_{p,\,t,\,m}$$
$$= (\mu_k)_o - (\mu_k)_s$$

The results of these important operations concerning the reversible transference of matter at constant temperature are therefore expressed in the clearest manner by means of the potentials of Gibbs.

Reference has already been made to the graphical representations of thermodynamic properties discussed in Gibbs' first two papers. This geometrical method was much developed in the section of his memoir on the equilibrium of heterogeneous substance, entitled "Geometrical Illustrations." This close alliance of geometry with analysis has had the most profound effect on the subsequent development of the theory and practice of heterogeneous equilibria. It is indeed no exaggeration to say that Gibbs' work in this field has given rise to a great and important branch of science. A good example of the power of this method as applied to the equilibrium of solids and solutions may be seen in the paper published in 1893 by van Rijn van Alkemade. It is now a well-known matter of history how Bakhuis Roozeboom, the first to undertake an extensive experimental exploration of this field, had his attention drawn by van der Waals to the theoretical researches of Gibbs, and how Roozeboom found in this work the sure foundation and guide which he required. Under the influence of van't Hoff and Roozeboom, the study of heterogeneous equilibria, treated chiefly from the graphical standpoint, rapidly developed in Holland, and from

there extended to every part of the world. Since the death of Roozeboom, the greatest exponent of this branch of science has been Schreinemakers, who, being a gifted mathematician as well as an experimental investigator, has been able to develop and apply the methods of Gibbs in the fullest possible manner. Van't Hoff, by his work on the oceanic salt deposits of the Stassfurth district, created the science of experimental mineralogy as a special branch of the theory of heterogeneous equilibria. Nowhere in the world has this science achieved a more splendid development than in the Geophysical Laboratory at Washington. The same theory has revolutionized the study of alloys and much of the science of metallurgy. The glowing iron and steel which pour daily from thousands of furnaces depend for their intelligent understanding and control on the impulse sent forth into the world from the quiet study at Yale University. Has there ever been a greater example of that eternal truth, that from the finest theory is born the finest practice? During the Great War, the safety of Great Britain and her Allies depended at a very critical moment on the ability of an Englishman, Dr. Francis Arthur Freeth (Chief Chemist to the celebrated firm of Messrs. Brunner, Mond and Co.), rapidly to devise well-founded and scientifically controlled processes for the daily manufacture of enormous quantities of ammonium nitrate from mixtures of other salts. Freeth, a devoted and expert disciple of Gibbs, Roozeboom, and Schreinemakers, solved the problem by means of the graphical methods founded on the thermodynamical theory of heterogeneous equilibria. Thus the invisible links of human thought reached across the years from the peaceful study of an American mathematician almost to the very mouths of the guns.

The work and inspiration of Gibbs have thus produced not only a great science, but also an equally great practice. There is, to-day, no great chemical or metallurgical industry which does not depend, for the development and control of a great part of its operations, on an understanding and application of thermodynamic chemistry and the geometrical theory of heterogeneous equilibria.

It is curious and interesting to observe how strongly, during the last thirty or forty years, the great Dutch school of physicists and chemists has been inspired and influenced by the work of Gibbs. One might almost say that the experimental study of the

equilibria of coexistent phases of matter is a Dutch science. Many instances might be given besides those already mentioned, but it must suffice here to refer to the investigations of Kuenen on the phenomena of evaporation and condensation in mixtures and to those of Cohen on the allotropic states of matter. It is, perhaps, scarcely necessary to mention that the great work of van der Waals and of Kamerlingh Onnes has been largely concerned with the more physical aspects of this field of investigation.

There is no finer monument to the influence of this side of Gibbs' work than the "Heterogene Gleichgewichte," begun by Roozeboom and carried on by Schreinemakers and Büchner. Many other useful and interesting books on this subject (such as those of Findlay, Jänecke, Kremann, Boeke, Clibbens, Rivett, etc.) have appeared, but it is pleasant to recollect that the first book to appear in this field—and a very interesting one, too—was written by a fellow countryman of Gibbs, namely, Wilder Bancroft.

In considering the effects of additional equations of condition on the general thermodynamical conditions of equilibrium, Gibbs dealt with the case in which two homogeneous fluid masses are separated by a diaphragm capable of supporting an excess of pressure on one side and permeable only to some of the components. It followed at once from the principles which he had established that the potential of a permeating component must be the same in both masses. Let us suppose, for example, that a pure liquid solvent is separated by a diaphragm freely permeable to the solvent from a solution of a non-permeating solute in the same solvent. Denoting the solvent and solute components by the numbers 1 and 2, respectively, and the solvent and solution phases by the letters A and B, respectively, then for equilibrium

$$(\mu_1)_A = (\mu_1)_B.$$

This follows at once from the equation of equilibrium

$$(\Sigma \mu dm)_A + (\Sigma \mu dm)_B = 0$$

The osmotic pressure $P(= p_B - p_A)$ can be at once expressed in a perfectly general form from Gibbs' equation

$$vdp = sdt + m_1 d\mu_1 + m_2 d\mu_2$$

applied to the variation of pressure with composition in the solu-

tion phase, for, since at constant temperature t and μ_1 remain constant in this case,

$$vdp = m_2 d\mu_2, \text{ i.e., } dp = c_2 d\mu_2$$

and therefore

$$P = \int_o^{c_2} c_2 d\mu_2 .$$

From the Gibbs-van't Hoff equation for components present in very small amount, namely, $\mu_2 = Rt \log c_2 + k$, where k is a function of pressure and temperature, it follows at once (neglecting the very small change of k with pressure) that $P = Rtc_2$. If we introduce the Lewis concept of fugacity, writing

$$\mu_2 = Rt \log f_2 + k$$

and also that of the fugacity coefficient γ_2 defined by the equation $f_2 = \gamma_2 c_2$, we can write Gibbs' equation in the general forms

$$P = Rt \int_o^{f_2} \frac{df}{\gamma}$$

or

$$P = Rtc_2 + Rt \int_o^{c_2} c\, d(\log \gamma),$$

since

$$df = \gamma dc + c d\gamma .$$

Furthermore, if we introduce an osmotic coefficient j_2, defined by the equation

$$P = j_2 Rtc_2$$

it follows that

$$j_2 - 1 = \frac{1}{c_2} \int_o^{c_2} c\, d(\log \gamma), \text{ or } j_2 = \frac{1}{c_2} \int_o^{f_2} \frac{df}{\gamma} = \frac{\gamma_2}{f_2} \int_o^{f_2} \frac{df}{\gamma} .$$

From the last equation, it follows that

$$\frac{d}{df}\left(\frac{jf}{\gamma}\right) = \frac{1}{\gamma}, \text{ or } 1 - j = \frac{dj}{d \log f} - \frac{j}{\gamma} \frac{d\gamma}{d \log f} .$$

These remarks will be sufficient to indicate that Gibbs in 1875–1878 had established the thermodynamical theory of osmotic pressure on a secure and general basis. In combination with the discovery subsequently made by van't Hoff, the approximate expression applicable to dilute solutions was firmly established. In a letter written to the English journal, *Nature*, in 1897, Gibbs showed how the approximate expression for the osmotic pressure of a sufficiently dilute solution could be readily obtained from his general differential equation and the (approximate)

expression for the potential of a volatile solute which held valid within the limits of Henry's law. When we consider the part played by the concept of osmotic pressure in the earlier and very important development of the theory of dilute solutions, we cannot but feel the greatest admiration for the investigations of Gibbs in this field. If later investigators of the osmotic pressures of solutions which are not sufficiently dilute had gone back to the work of Gibbs, much confusion and error would have been avoided.

It is perhaps truer of Gibbs than of any other man that many of the results which he obtained have been made, unconsciously or subconsciously, the starting points of series of investigations by later workers in the field of thermodynamic chemistry. An example of this sort, in which the writer of the present article must plead guilty, is seen in Gibbs' treatment of the equilibrium across a semi-permeable diaphragm. Let us suppose that the diaphragm is permeable to a linearly correlated group of components, *i.e.*, a number of components which can pass through the diaphragm only together and in amounts which stand to each other in a constant proportion. We may express this condition by the equations $\left(\frac{dm_1}{a_1}\right)_A = \left(\frac{dm_2}{a_2}\right)_A =$ etc., where a_1, a_2, etc., are constant positive quantities and A refers to the fluid phase on one side of the diaphragm. A similar series of equations holds for the B-phase, the quantities a_1, a_2, etc., being taken negatively. The general equation of equilibrium

$$(\Sigma \mu dm)_A + (\Sigma \mu dm)_B = 0$$

then gives at once the relation obtained by Gibbs

$$(\Sigma a \mu)_A = (\Sigma a \mu)_B$$

where the signs of summation apply to the correlated group of components.

In 1911, the present writer investigated this phenomenon in the case where the linear correlation is due to the operation of electrostatic forces, which control the simultaneous diffusion across the semi-permeable diaphragm of electrically charged (ionized) components. For example, if we consider the diffusion of electrically equivalent masses of the ions H^+ and Cl^- and refer the potentials to these equivalent masses, we obtain the relation

$$(\mu_{H^+} + \mu_{Cl^-})_A = (\mu_{H^+} + \mu_{Cl^-})_B$$

which in terms of fugacities reduces to the form

$$(f_{H^+} \cdot f_{Cl^-})_A = (f_{H^+} \cdot f_{Cl^-})_B.$$

If there were no other ions present, this equation would reduce, of course, to an identity; but if we suppose, for example, that in one of the two fluid phases there is present the ionized salt B^+Cl^-, whose cations B^+ cannot diffuse across the diaphragm, we perceive at once that in the equilibrium state the concentrations of the hydrogen and chlorine ions will be severally different in the two solutions.

The foregoing equation can be written in the form

$$(\gamma_{H^+} \cdot \gamma_{Cl^-})_A \cdot (c_{H^+} \cdot c_{Cl^-})_A = (\gamma_{H^+} \cdot \gamma_{Cl^-})_B \cdot (c_{H^+} \cdot c_{Cl^-})_B$$

As is now well known, the operation of interionic (electrical) forces limits the sufficiently exact applicability of the Gibbs-van't Hoff equation, $\mu = Rt \log c + k$, in the case of ionized components to extremely great dilutions. Hence it is only in such cases that we can write with sufficiently high approximation.

$$(c_{H^+} \cdot c_{Cl^-})_A = (c_{H^+} \cdot c_{Cl^-})_B$$

In spite of this difficulty, the roughly approximate equations relating to the distribution of ions across semi-permeable membranes have been of considerable value, and in the hands of Jacques Loeb, O. Warburg, D. D. van Slyke, and Laurence J. Henderson have already contributed to the advance of physiological science. In particular, these ionic distribution equations have supplied a missing link in the complicated chain of blood equilibria, the theory of which has now been brought to a state of very high development by the work of Henderson and van Slyke. The approximate ionic distribution equations have also contributed very considerably to the study of protein sols and gels, as is shown by the investigations of Procter and Wilson and of Loeb and his collaborators. Once again we can perceive the mighty inspiration and influence of Gibbs extending the invisible empire of his thought across half a century of scientific development.

In a recent paper dealing with the physico-chemical aspects of blood equilibrium, Laurence J. Henderson and his collaborators have conferred on the present writer the incomparable honor of associating his name with that of Gibbs in connection with the equations of ionic distribution. Such cases of " membrane equi-

librium," where in the state of equilibrium any ionic or electrically charged component for which the membrane is permeable possesses unequal values of its chemical potentials in the two homogeneous fluids, must result in a difference of electrical potential on either side of the membrane. The method of Gibbs enables us to obtain a perfectly general expression for this potential difference. Thus, in the example already given, we may imagine a reversible variation of the equilibrium system in which δn mols of hydrogen ion are transferred from the solution B to the solution A. If V_A and V_B denote the electrical potentials of A and B, respectively, and G the quantity of electricity associated with 1 gram of an ion, then

$$\delta u = t\delta s - p\delta v + \{ (\mu_H)_A - (\mu_H)_B \} \delta n + G(V_A - V_B)\delta n$$

For constant temperature t and constant pressure p, this gives

$$\frac{\delta F}{\delta n} = (\mu_H)_A - (\mu_H)_B + G(V_A - V_B)$$

Hence for equilibrium at constant temperature and pressure

$$V_A - V_B = \frac{1}{G} \{ (\mu_H)_B - (\mu_H)_A \}$$

For very dilute solutions this general equation may be expressed in the approximate form:

$$V_A - V_B = \frac{Rt}{G} \log \frac{(C_H)_B}{(C_H)_A}$$

The method employed in deducing these equations is precisely that used by Gibbs in his discussion of the theory of a perfect electrochemical apparatus, so that we have here another example of the importance and generality of his thermodynamical investigations.

Considerable importance attaches to cases of heterogeneous equilibrium where the coexistent phases are subject to unequal stress. Gibbs gave a very exhaustive treatment of certain problems of this character, but it will be sufficient for the purposes of this article to indicate very briefly the method which we can apply to a simple type of case. Gibbs' fundamental equation, $vdp - sdt + \Sigma m d\mu$, reduces in the case of one component at constant temperature to the simple form

$$vdp = md\mu \text{ or } v_o dp = d\mu$$

where v_o = specific volume. Let us consider the case of a pure

liquid or solid in equilibrium with its vapor, the condensed phase being subject to a uniform pressure P. From the equation of Gibbs we have then

$$\left(\frac{d\mu_o}{dP}\right)_t = v_o$$

where μ_o is the potential of the condensed phase (solid or liquid). If μ be the potential of the vapor, $\mu_o = \mu$ and if p denote the vapor pressure, then, if p be not too great, $\mu = Rt \log p + k$, so that we can write

$$\left(\frac{d \log p}{dP}\right)_t = \frac{v_o}{Rt}$$

where v_o = the molar volume of the condensed phase. We can extend this equation to the case of dissociation-equilibrium. Consider, for example, the equilibrium $S_1 = S_2 + G$, where S_1 and S_2 are pure solids and G a pure gaseous phase. Let us suppose that the chemical equation is $aS_1 + bS_2 = cG$. For equilibrium $a\mu_1 = b\mu_2 + c\mu_3$ where μ_1, μ_2 and μ_3 are the potentials per mol of S_1, S_2 and G, respectively. Hence, differentiating at constant temperature,

$$a\frac{d\mu_1}{dP} = b\frac{d\mu_2}{dP} + c\frac{d\mu_3}{dP}$$

where we suppose that the solid phases are subjected to the uniform pressure P. From the previous result it follows that

$$aV_1 = bV_2 + Rtc\frac{d \log p}{dP}$$

where p is the pressure of the gaseous phase.
Hence

$$\left(\frac{d \log p}{dP}\right)_t = \frac{aV_1 - bV_2}{cRt}$$

This differential equation shows how the dissociation-pressure p varies with the pressure P applied to the condensed phases. A similar method can be applied to the case where the phase of variable concentration is liquid. As is well known, the effects of unequal stress have been dealt with theoretically and practically by Le Chatelier, Tammann, and others, and their importance in geological and other phenomena pointed out by various investigators. The thermodynamic theory of all such phenomena is contained (whether explicitly or implicitly) in the work of Gibbs.

Gibbs devoted a large part of his paper on the equilibrium of heterogeneous substances to a comprehensive and detailed discussion of the influence of "surfaces of discontinuity" on such equilibria. By the term "surface of discontinuity" Gibbs meant, as he explained, the exceedingly thin non-homogeneous films which separate homogeneous or nearly homogeneous masses. Although Lord Kelvin had already made some important contributions to the theory of the heat effects which accompany the reversible extension of surfaces in the case of one component systems, the generalized treatment employed by Gibbs may without exaggeration be said to have created a new branch of science, namely, the thermodynamical theory of capillarity. The fundamental idea underlying Gibbs' method of investigation was the introduction of terms denoting the *superficial densities* of energy, entropy and of the several component substances. He defined this superficial density as the *excess*, per unit of interfacial area, of the quantity in question in the interfacial film, over and above the amount which would have been present if the homogeneous masses had extended without alteration of any sort right up to the dividing surface. In this way he obtained for the equilibrium state fundamental equations relating to the interface, as, for example:

$$u_s = ts_s + \sigma + \mu_1\Gamma_1 + \mu_2\Gamma_2 + \text{etc.}$$

$$d\sigma = -s_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \text{etc.}$$

where u_s and s_s denote the interfacial excess amounts (superficial densities) of energy and entropy, respectively, Γ_1, Γ_2, etc., the interfacial excess amounts of the several components, μ_1, μ_2, etc., the potentials of the components in the homogeneous masses present in equilibrium and σ a quantity which will generally be sensibly equal to the interfacial tension as experimentally measured. If the densities of one of the components be very different in the two homogeneous masses, it will be generally possible, as Gibbs showed, to place the "mathematical" dividing surface with respect to which the quantities in the equation are exactly defined, in such a position that the value of Γ for this component becomes zero and that nevertheless this position coincides sensibly with the physical interface. We cannot do better than quote the words used by Gibbs in dealing with a special example. "If liquid mercury meets the mixed vapors of water and mercury in a plane

surface, and we use μ_1 and μ_2 to denote the potentials of mercury and water, respectively, and place the dividing surface so that $\Gamma_1 = 0$, *i.e.*, so that the total quantity of mercury is the same as if the liquid mercury reached this surface on one side and the mercury vapor on the other without change of density on either side, then[1] $\Gamma_{2(1)}$ will represent the amount of water in the vicinity of this surface, per unit of surface, above that which there would be if the water vapor just reached the surface without change of density, and this quantity (which we may call the quantity of water condensed upon the surface of the mercury) will be determined by the equation

$$\Gamma_{2(1)} = -\left(\frac{d\sigma}{d\mu_2}\right)_t.$$

If the pressure in the mixed vapors conforms to the law of Dalton, we shall have for constant temperature $dp_2 = \gamma_2 d\mu_2$ where p_2 denotes the part of the pressure in the vapor due to the water vapor and γ_2 the density of the water vapor. Hence we obtain

$$\Gamma_{2(1)} = -\gamma_2\left(\frac{d\sigma}{dp_2}\right)_t.$$

For temperatures below 100° C. this will certainly be accurate, since the pressure due to the vapor of mercury may be neglected."

With these words Gibbs introduced into science a very important method of determining the interfacial accumulation of a substance which lowers the interfacial tension at a boundary between two fluid phases in a system of two components. Many investigations have been founded on this part of Gibbs' work, which has proved to be of fundamental importance in various branches of science.

The general equation of Gibbs,

$$\Gamma = -\frac{d\sigma}{d\mu},$$

may be written also in the general form

$$\Gamma = -\frac{1}{Rt}\frac{d\sigma}{d(\log f)},$$

if we introduce the Lewis fugacity function f as defined by the equation $\mu = Rt \log f + k$. For solutions which are "ideal" in

[1] The symbol $\Gamma_{2(1)}$ denotes the superficial excess amount of water (component 2) with respect to the dividing surface so placed that $\Gamma_1 = 0$.

behavior or which are sufficiently dilute to permit the use of the Gibbs-van't Hoff equation, $\mu = Rt \log c + k$, we can also write,

$$\Gamma = -\frac{c}{Rt}\frac{d\sigma}{dc},$$

which is the form of the equation that has been most frequently employed. The question arises as to how Γ varies with c at constant temperature, since as c increases it is found by experiment that the numerical value of $\frac{d\sigma}{dc}$ diminishes. It was first pointed out by S. R. Milner that, except in very dilute solutions, σ could be expressed as a linear function of $\log c$ in the case of certain very "surface active" substances. This would indicate that in these cases Γ attains a limiting value which is independent of c. This point was much elucidated by I. Langmuir's discussion of the measurements of B. de Szyszkowski, who had determined the surface tensions of aqueous solutions of a number of organic acids of the aliphatic series. The data of Szyszkowski can be expressed by the equation

$$\sigma = \sigma_0 - B \log\left(\frac{c}{A} + 1\right)$$

where the constant B is independent of the acid used. From this it follows that

$$\frac{d\sigma}{dc} = -\frac{B}{c + A},$$

and hence from Gibbs' equation that

$$\Gamma = \frac{B}{Rt} \cdot \frac{c}{c + A}.$$

We see therefore that, with increasing c, Γ approaches the limiting value $\frac{B}{RT}$, which is the same for all the acids used, namely, propionic, butyric, valeric, and caproic acids.

In recent years very great interest has attached to the theory of unimolecular surface layers, due initially to Lord Rayleigh and much advanced by the researches of Marcelin, Devaux, Langmuir, and Adam. In this connection, the important question has arisen as to whether the limiting or "saturation" values of Γ, as calculated by means of the equation of Gibbs, would lend any support to the view that the surface accumulation consists in the building up of a unimolecular layer of the surface-concentrating com-

ponent. Having determined the limiting value of Γ, as indicated above, and knowing the value of the Avogadro number, namely, 6.06×10^{23} molecules per gram mol, it is easy to calculate the corresponding surface area per molecule of the excess surface accumulation. The following table gives some of the results obtained in this manner.[2]

Surface Active Components.	Interface.	Area per Molecule in Sq. Cm. $\times 10^{15}$	Observers.
Propionic, butyric, valeric and caproic acids ..	Water/air	31	I. Langmuir (Szyszkowski)
Butyric acid.....	Water/air	36	W. Harkins
Nonylic acid	Water/air	ca. 26	F. G. Donnan J. T. Barker
Aniline	Water/air	34	I. Langmuir (Worley)
Butyric acid	Water/mercury	36	W. D. Harkins
Potassium palmitate.....	Water/mineral oil	30	E. L. Griffin
Methyl acetate.....	Air/mercury	27	T. Iredale
Dimethylaniline.....	Benzene/water	34	J. H. Mathews and A. J. Stamm

The similarity of these values and the fact that they are of the same order of magnitude as the values for molecular cross-sections determined by Langmuir and by Adam by a quite different method, seem to lend strong support to the theory of Langmuir that the maximum surface accumulation in these cases consists in the formation of a unimolecular layer of molecules at the interface.[3] Apart, however, from their bearing on the question of the possible formation of unimolecular layers, the equations of Gibbs relating to the surface concentration of components have been of the greatest importance in many subsequent investigations concerning the formation of surface films, foams, emulsions, and various disperse states of matter. Whatever may prove to be the complete explanation of the group of complex phenomena usually classified together under the heading of "adsorption," the thermodynamical theory of Gibbs has provided in the past at least one sure and safe foundation on which to build. In this connection,

[2] In two of these cases the interfacial excess has been directly measured.

[3] It will be noticed that if the interfacial accumulation consists in the formation of a unimolecular layer, the difficulty about the position of the "dividing surface" largely disappears.

it is of interest to ascertain, as has been recently done by Haber, under what conditions the empirical adsorption isothermal of Freundlich may be deduced from the simplified equation of Gibbs. Writing the equation

$$\Gamma = -\frac{1}{Rt}\frac{d\sigma}{d\log c}$$

in the form

$$\Gamma = -\frac{1}{Rt}\cdot\frac{d\sigma}{d\Gamma}\cdot\frac{d\Gamma}{d\log c}$$

it easily follows that

$$Rt\frac{d\log c}{d\log\Gamma} = -\frac{d\sigma}{d\Gamma}$$

If σ can be expressed, to a first degree of approximation, as a linear function of Γ, then $\frac{d\sigma}{d\Gamma}$ is a constant (to the same degree of approximation) and we have, at constant temperature

$$\log\Gamma = n\log c + \log A,$$

where n and A are constants. This gives for dilute solutions and surface active substances Freundlich's adsorption isotherm, $\Gamma = Ac^n$.

For variations in the composition of a single phase at constant temperature and pressure, the equation of Gibbs

$$vdp = sdt + \Sigma m d\mu$$

leads to the result

$$\Sigma m d\mu = 0.$$

An analogous equation applicable to the interface follows from the equation

$$d\sigma = -s_s dt - \Sigma\Gamma d\mu$$

since, for such variations of composition of the two adjacent phases as occur at constant temperature and do not change the value of σ, it follows that

$$\Sigma\Gamma d\mu = 0$$

which for a two-component system reduces to

$$\Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 = 0.$$

The foregoing considerations alone suffice to show the important influence which even a very small part of Gibbs' work in the domain of surface action and surface equilibrium has exerted

on later investigations. So profound and extensive, however, was the reasoning of Gibbs in this field that even to-day not a hundredth part of the rich crop has been harvested. Even a bare enumeration of the questions with which he dealt would require much time and space. Among some of the simpler problems, the solution of which has been important for later work, one may note in passing the equations for the Lippmann electrocapillary effect and the general expressions for the thermal and mechanical effects associated with the extension of interfaces. In spite, however, of the great assistance and inspiration which later investigators have obtained from Gibbs' thermodynamical theory of interfaces, it is fully as proper to speak of the influence which this theory will exert on future research as of that which it has already exerted in the past.

The study of the electromotive forces of reversible galvanic cells has proved of great importance in the development of physico-chemical science during the last thirty or forty years. The principles of thermodynamics have been the only sure guides in this field of investigation, and so there has grown up an important branch of science which may be called electrochemical thermodynamics. In the last part of his paper on the equilibrium of heterogeneous substance, Gibbs, with remarkable insight, not only laid the foundations of this branch of science, but showed in very considerable detail the manner in which its different types of problems could be solved. Before the investigations of Gibbs, physicists and chemists had believed that the energy in the form of electrical work supplied by a galvanic cell working at constant temperature was derived solely from the change in the internal energy of the physico-chemical system. Gibbs showed that the galvanic cell would in general give out heat to, or absorb it from, its surroundings, and that there was no simple relation of proportionality between the electrical work done and the decrease of internal energy. As Gibbs divined, the true equation is $du = dQ + dW_G + dW_p - (V_1 - V_2)de$, where du is the increment of the internal energy of the cell, V_1 and V_2 the electrical potentials of the electrodes, de the quantity of electricity passing through the cell, from electrode 2 to electrode 1, dQ the heat received from external bodies, dW_G the work done by gravity, and dW_p the work done by the pressures acting on the external surface of the apparatus. As the cell is supposed to work rever-

sibly, $dQ = tds$. Neglecting the term dW_G, which usually will be extremely small, and supposing the cell to be subjected to a uniform pressure p,

$$du = tds - pdv - (V_1 - V_2)\,de_1$$

where dv is the increase in volume of the cell (including its products of electrolysis) due to the passage of de units of electricity. The fundamental defect of earlier theories had been the neglect of the term tds. If the cell works at constant temperature and if the pressure p is not only uniform but constant, then, since in this case $dF = du - tds + pdv$, we have the very simple relationship $V_1 - V_2 = -\frac{dF}{de}$. Thus the electrical work $(V_1 - V_2)de$ done by the cell is equal, not to the decrease of the total internal energy of the cell, but to the decrease of the quantity F. This equation of Gibbs might well be described as the cornerstone of electrochemical thermodynamics. It would be difficult to exaggerate the importance of the part which it has played and still plays in chemical science.

Besides developing the general thermodynamic relations of the "perfect (*i.e.*, reversibly working) electrochemical apparatus," the investigations of Gibbs demonstrated the great value of his concept of the potential of a component. For, recollecting that $dF = \Sigma\mu dm$ for reversible variations of a system at constant temperature and pressure, we can write the former equation in the form $(V_1 - V_2)de = -\Sigma\mu dm$. Suppose, to take one of Gibbs' own examples, we have a reversible galvanic cell in which the electrodes are solid metallic zinc and a solution of zinc in mercury, respectively, the electrolyte being a solution of a zinc salt. Imagine a reversible variation in which de units of electricity pass from the zinc to the amalgam electrode, V_2 being the electrical potential of the former and V_1 of the latter. Then, since $dm = ade$ where a is a known constant quantity from Faraday's law, $\Sigma\mu dm = a(\mu_1 - \mu_2)\,de$, where μ_1 is the chemical potential of zinc in the amalgam and μ_2 the chemical potential of solid metallic zinc. Hence $V_1 - V_2 = a(\mu_2 - \mu_1)$. Thus we may write $\mu_1 = \mu_2 - \frac{E}{a}$ where E is the electromotive force of the galvanic cell, and so by measurements of E compare the chemical potentials of zinc in liquid amalgams of different concentrations (at the specified temperature and pressure).

These examples will suffice to show how completely Gibbs had laid down the solid basis of electrochemical thermodynamics. The famous letter written by him to Prof. W. D. Bancroft in May, 1899, shows how easily Gibbs could have arrived at all the results obtained subsequently by a host of investigators if his attention had not been concentrated on other subjects. Many of these results were laborious rediscoveries of Gibbs' principles, and were frequently expressed in a very inexact form. Nothing in the history of science is more remarkable than the way in which Gibbs in 1878 provided the electrochemical science of the succeeding generation with its thermodynamical *Principia*. Some years after the appearance of Gibbs' work, Helmholtz dealt with the calculation of the electromotive forces of reversible galvanic cells and in particular obtained an important differential equation correlating the electromotive force, its variation with temperature, and the decrease of internal energy of the physico-chemical system. In two letters which Gibbs wrote in 1887 to the Secretary of the Electrolysis Committee of the British Association for the Advancement of Science (Oliver Lodge), he explained to a rather unenlightened world the principles of electrochemical thermodynamics which he had established in 1878, and showed that Helmholtz's result followed naturally therefrom.

The very inadequate sketch of Gibbs' work and influence in one field of knowledge, which has been attempted in the foregoing pages, may perhaps suffice to show that he was the founder and creator of the science of physico-chemical thermodynamics. Like Lagrange and Hamilton, he was the great and profound mathematician (or mathematical physicist) who, utilizing the scientific advances of half a century and applying to them the full power and scope of deductive logic, so extended and generalized the results of his predecessors and contemporaries as to create a new foundation and a new starting point for human effort. At a time when the atomic and molecular theories were still comparatively undeveloped, the work of Gibbs gave to physical and chemical science a fresh impulse of the highest value and the greatest fruitfulness. The mighty wave of this impulse has extended to many allied fields and knowledge, to mineralogy, metallurgy and physiology, and to almost every branch of industrial practice.

In physiology, the power and value of thermodynamical

methods have been fully recognized only in comparatively recent times. Perhaps after another century of research in this science, there may come another Willard Gibbs, who will discover the fundamental equations of the living cell, where the unseen hand of the past seems to reach out and grip the future. But for that we shall require something more than linear differential equations. The power of rigorous deductive logic in the hands of a mathematician of insight and imagination has always been one of the greatest aids in man's effort to understand that mysterious universe in which he lives. Without the presence of this power, the experimental discoverer might wander in the fields and pick the wild flowers of knowledge, but there would be no beautiful garden of understanding wherein the mind of man can find a serene delight. The world owes an immense debt of gratitude to the possessors of this power, and to none more than to Josiah Willard Gibbs. So faithfully and wisely did he use the splendid gifts which Nature had bestowed on him, that after half a century of time his work remains a potent and living force. Of such work it is, and always will be, true that the eager hand of Time may add something, but can take nothing away.

The Structure of Graphite. J. D. BERNAL. (*Proc. Roy. Soc.*, A 740.)—"The X-ray analysis of graphite has lagged considerably behind that of the diamond. Bragg, in 1914, made a measurement of the spacing of the cleavage planes, finding it to be 3.42 Å.U. (hundred-millionths cm.), while Ewald, in the same year, took a Laue photograph of a crystal, perpendicular to the axis, confirming its hexagonal symmetry. The fuller interpretation of its structure was attempted by Hull and by Debye and Scherrer in 1917 by the powder method. Both were able to assign a structure to the element, but these structures have different lattices and belong to different crystal systems."

In the present determination Ceylon graphite was used. Crystalline fragments of it were mounted on a goniometer holder. X-rays fell upon the revolving crystal and the resultant diffracted rays were received upon a cylindrical photographic film, concentric with the crystal. "All the measurements from the photographs agree with the lattice suggested by Hull, namely, a hexagonal lattice." This is a right prism of length 6.8 Å.U. with regular hexagons for ends, a side being 2.4 Å.U. in length. There are four atoms of carbon to the unit cell. From a study of the intensities of the successive orders of the X-rays reflected a very definite idea of the structure was attained. "The atoms of carbon in graphite lie in planes in which

they form nets of hexagons. These nets are in successive planes, superposed so that half the atoms in one net lie normally above half the atoms in the net beneath, while the other half lie normally above the centres of the hexagons of this net. Alternate nets lie atom for atom normally above each other. It will be seen that this model, while it accepts Hull's lattice, has the carbon atoms arranged in plane nets, as in the model of Debye and Scherrer, so that it agrees and disagrees with both equally."

The carbon atoms are closer together in graphite than in the diamond. The cleavage spacings of artificial graphite were found to differ from those of the natural material by no more than .3 per cent.

G. F. S.

Registration at Sea-level of the Radiation Characteristic of High Altitudes. G. HOFFMANN. (*Physik. Zeit.*, Jan. 1, 1925.)—"The penetrating radiation observed near the earth by means of customary closed ionization chambers is assumed in accordance with previous results to be composed of γ-radiation coming from radio-active substances distributed in adjacent matter and of a radiation of special character, the radiation of high altitudes (Hoehenstrahlung). The γ-radiation from the vicinity of the instrument varies considerably with locality and, in addition, is subject to change with time in consequence of changes of atmospheric conditions. This two-fold modification in the value of one component makes it difficult to follow the course of the other. For this reason it is necessary to carry out observations in high mountains, where the proportion of high altitude radiation is several times as large as in the lowland. This task has been undertaken in sundry places. Kohlhoerster from his measurements in July, 1923, above glaciers in the Alps, thought he could detect with certainty a definite daily period in the high altitude radiation. He further concluded, though reserving the right to revise his deductions in the light of later and more accurate observations, that the radiation under examination came from limited portions of the vault of the sky." The same investigator has shown that the high altitude radiation possesses a power of penetration about ten times as great as that of the hardest γ-rays derived from radio-active substances. At sea-level the high altitude radiation produces one pair of ions per second in one c.c. of air.

The author has planned an ionization chamber with a view to eliminating the effect of the radiation coming from its walls. This he surrounds with a panoply of lead 12 cm. thick. Through this sheath only 1 per cent. of the γ-radiation from radium can penetrate, whereas 60 per cent. of the high-altitude radiation passes through it into the ionization chamber. The motion of the pointer of the electrometer was registered photographically. From the traces obtained no confirmation was derived for the existence of a diurnal period of the radiation.

G. F. S.

CHANGES OBSERVED IN THE DIRECTION OF RADIO SIGNALS AT THE TIME OF THE ECLIPSE OF JANUARY 24, 1925.*

BY

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As a part of the program of eclipse observations at Ithaca, N. Y., records were kept during the morning hours of January 23, 24 and 25, 1925, of the apparent directions of Stations WGY (Schenectady) and WEAF (New York) as indicated by radio direction finders. While an effect due to the eclipse is indicated in the case of the signals from both stations, a discussion of the probable cause of the observed changes will be more profitable when all of the numerous radio observations during the eclipse, including measurements of intensity as well as of direction, are available. We are offering the observations plotted on the accompanying graph as a contribution to the data for such a discussion. The results are of interest, however, aside from their bearing on the eclipse effect, for not many observations of this kind extending over a considerable period, and under different atmospheric conditions, have been published, and those that have been published have usually been made with long waves.

In the observations on Station WEAF a super-heterodyne receiving set was used, with a loop antenna of six turns, one metre square, which could be rotated about a vertical axis. Settings were made on the 250-cycle tone to which the carrier wave was modulated. The sharpness of the setting for minimum sound varied greatly. During the early morning hours, if high amplification was used, it was often impossible to find any point where the sound completely died out. For this reason the amplification was adjusted to give a rather narrow region of zero sound and settings were made in pairs, approaching the zero from both sides. The average of each pair of readings is plotted. The changes in direction were often much more rapid than is indicated by the curves, sometimes occurring with such rapidity that it was impossible to make settings. When steady conditions prevailed, however, the settings agreed within two degrees or less.

* Communicated by Professor Merritt, Head of the Department.

For the observations on Station WGY a four-tube receiving set was used in which one stage of radio amplification was followed by a regenerative circuit with one detector tube and two stages of audio amplification. The first tube was balanced to prevent reradiation. The second tube was allowed to oscillate and to give a beat tone of about 1000 cycles with the carrier wave from WGY. The loop antenna was similar to that of the other receiving set. With steady conditions this arrangement gave extremely sharp settings, which could be repeated with variations of less than one degree.

The observations were made in a barn about a mile and a half directly east of Ithaca. A ditch digging machine containing a considerable amount of metal stood about twenty metres east of the barn and an east and west telephone line was at a distance of about 100 m. to the south. While these sources of disturbance might perhaps alter the settings by a small fraction of a degree, they could hardly have an appreciable effect on the time variations in the direction of the waves. There were no disturbances from regenerative receiving sets or other local causes. The north and south direction was determined by a pocket compass, due allowance being made for the fact that the declination at Ithaca is 8° to the west. An error of 2° in the absolute direction is not unlikely.

The weather conditions over central New York during the forenoon of each of the three days on which observations were made are given below:

January 23rd.

Cloudy. Temperature −18° C. (0° F.). Barometer reduced to sea-level 773 mm. (30.45 in.). Wind NW.

Barometric high (780 mm.) just north of Lake Superior. Low (736 mm.) over Nova Scotia. Pressure gradient 2.5 mm. per 100 km. toward east.

January 24th.

Clear. Temperature −18° C. (0° F.). Barometer (reduced) 776 mm. (30.55 in.). Wind SW.

Barometric high (777 mm.) over Norfolk, Va. Low just N. of Lake Superior (758 mm.) and east of Nova Scotia. Pressure gradient 1.8 mm. per 100 km. toward N. and NW.

January 25th.

Heavy Clouds. Temperature −1.5° C. (30° F.). Barometer (reduced) 766 mm. (30.15 in.). Wind SW.

Barometric high (777 mm.) NW. of Lake Superior, and S. of Norfolk, Va. (770 mm.). Pressure gradient 0.

Probably the most striking thing about the results obtained is the magnitude and the rapidity of the direction changes observed. Sudden variations of nearly equal magnitude have been recorded by Taylor [1] in the case of signals from New Brunswick (13,600 m.) received at night in Washington. Large shifts have also been observed at Meudon [4] on waves received from Hanover. But most of the published accounts of direction changes report much smaller shifts. In the observations of Kinsley and Sobey,[2] which were made on signals from both arc and spark stations and with wave-lengths ranging from 960 m. to 17,300 m., the maximum shift scarcely exceeded 15°. Pickard's measurements [2] on the long wave signals from Nauen, Bordeaux, and San Diego (the latter over land) show only slow variations whose maximum amplitude is about 5°.

Very little is known regarding the dependence of these erratic direction changes upon atmospheric conditions, wave-length, and the various other conditions which may affect the transmission of electric waves. All observers agree, however, that disturbed conditions and large changes in both direction and intensity are more likely to be found at night. Taylor [1] found that variations in direction were much greater in the case of long continuous waves than in the case of the shorter waves from spark stations and this conclusion was confirmed by Kinsley and Sobey.[2] Taylor explains the relative steadiness of the readings of short-wave direction finders as the result of the fact that they have usually been used on damped waves, which do not permit of definite and persistent interference patterns. Observations on short undamped waves, reported by Taylor but not yet published, are in agreement with this explanation since large erratic variations in direction were found for waves in the broadcasting range of wave-lengths (200 m. to 600 m.).

Pickard's observations on the long undamped waves from Nauen, Bordeaux, and San Diego not only showed extremely small variations in direction, in spite of the great wave-length, but also indicated very little difference between day and night. The difference between Pickard's results and those obtained by Taylor [1] with signals of equally great wave-length from New Brunswick, may be due to the fact that the route followed by the waves from New Brunswick to Washington is, roughly speaking, parallel to the coast line and to a considerable extent over land,

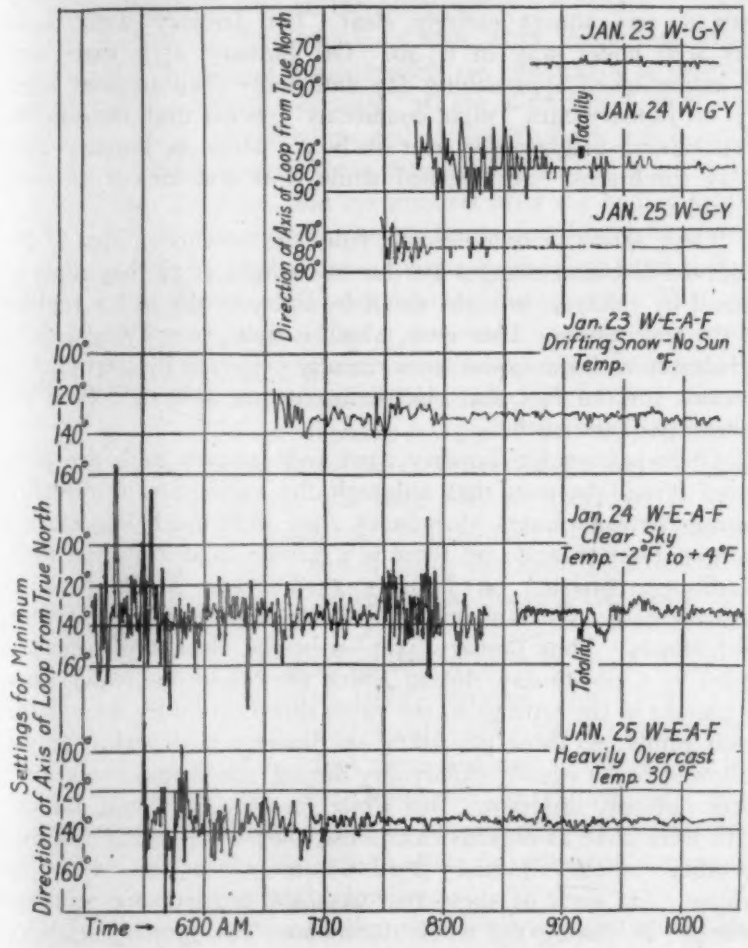
while Pickard's observations, except in the case of San Diego, were made on waves transmitted altogether over water. It seems to be generally agreed that direction finding over water is more reliable than over land. In view of the complexity of the whole problem, the observations thus far recorded seem quite inadequate for its solution and one is constrained to agree with Pickard that "it is only through an accumulation of additional data that we can hope to correlate these variations in direction and intensity with meteorological and other terrestrial elements, and in this way arrive at an understanding of their causes."

Since our observations on Station WEAF began at least an hour, and in one case two hours and a half, before sunrise, these observations bring out in a very striking way the change that occurs in the conditions affecting direction determinations during the transition from night to day. Night conditions are characterized by large and extremely rapid changes in direction. In several cases on January 24th and January 25th, changes of more than 90° occurred within a minute and the amplitude of the variations about the mean was at times as great as 80°. As the time of sunrise approaches the variations become less, and for a time the readings are fairly constant. But on January 23rd and January 24th a second period of disturbance began at sunrise and lasted for about forty to fifty minutes. On January 25th this second period of disturbance was not observed. When day conditions are fully established the readings are much more steady and although a sudden shift of as much as 5° occasionally occurs, the variation from the mean rarely exceeds 3°.

Since Station WGY did not begin transmitting until 7:30 A.M., it was not possible in the case of this station to get settings before sunrise. The curves therefore show only the final stages of the transition from day to night. It will be noticed that when day conditions are established the settings for WGY are more nearly constant than those for WEAF. We have no way of knowing whether the disturbances before sunrise are as great for the short waves of Station WGY (337 m.) as for the longer waves (462 m.) of Station WEAF. But the same tendency is shown for night conditions to persist after sunrise. In fact, on January 25th, when this persistence of night conditions seems to be absent for WEAF, it is clearly shown in the observations on signals WGY.

One of the most striking points brought out by these observations is the variation from day to day in the hour at which day conditions are established. On January 23rd the deflections

FIG. 1.



became steady for WEAF at 8 A.M. On January 24th, at 8:35; and on January 25th at 7:30. The persistence on January 24th of the disturbed conditions that are usually characteristic of darkness until an hour after sunrise is confirmed by the plot for

WGY on that day, where steady conditions were not reached until even later (8:50).

The difference between the curves for January 24th and 25th is made more striking by the fact that while on January 25th the sky was completely covered with clouds, on January 24th it was almost entirely clear. On January 24th dawn was well under way at 6:40. On January 25th there was no indication of approaching day until more than an hour later. Yet on January 24th "night conditions" persist until the sun has been shining brightly for over an hour; while on January 25th "day conditions" are reached while it is still almost as dark as midnight!

There seems to be no escape from the conclusion that if the observed direction changes are due to sunlight at all they must be caused by changes, brought about by light, in the *upper* regions of the atmosphere. This view, which is that generally held, is in agreement with the explanation recently proposed by Larmor [5] to account for the fact that electric waves are able to follow the curvature of the earth.

If the curves for January 23rd and January 24th are compared it will be seen that although the variations in direction during the early hours of January 23rd were much less marked than on January 24th, yet there is a definite indication that night conditions persisted on January 23rd nearly as long as on January 24th. On January 23rd the sky was completely covered with clouds. Thus January 24th—a bright, clear day—was preceded by a cloudy day, during which the conditions which cause variations in the settings of the radio direction finder were somewhat similar to those prevailing on January 24th; while it was followed by an equally cloudy day during which these conditions were radically different. But while January 23rd and January 25th were alike as regards cloudiness, they were widely different in other respects. January 23rd was as cold as the day of the eclipse. On each of these two days the temperature remained near 0° F. during the whole forenoon. On January 25th the temperature had risen nearly to the freezing point. The barometric pressure was high on all three days, but it was lower on January 25th than on either of the other two days; and the pressure gradient, which was steep on January 23rd and January 24th, was practically zero over New York State on January 25th.

Insofar as it is justifiable to draw conclusions at all from so few data, it appears that the persistence of night conditions after sunrise is associated with high barometric pressure and a large pressure gradient.

Evidence of what appears to be an effect due to the eclipse is shown especially well in the observations on WEAF. Night conditions persisted until half an hour after the eclipse began. But for an equal period before totality the conditions, as indicated by the nearly constant settings of the direction finder, were unusually steady. Toward the end of totality there was a sudden shift in direction toward the south, followed by a quick return to the normal reading. But six minutes after the end of totality a systematic drift toward the south began and for eight minutes the settings indicated that the signals were coming from a direction 15° south of the true direction of New York. This shift to the south was followed by a somewhat smaller shift to the north and thirty-five minutes after totality the readings had returned to their normal mean value. During the time that day conditions prevailed on January 23rd and January 25th there were many erratic shifts in direction; but these were of short duration and the largest was only half as great as the eight-minute shift to the south which followed totality. We feel, therefore, that this shift, and probably the shift to the north that followed it, are to be referred to changes resulting from the eclipse.

In the case of the observations on signals from WGY, the evidence of an eclipse effect is less striking. The curves show, however, that beginning four minutes after totality erratic shifts in direction occurred and that these persisted for thirty-five minutes. Both before and after this period the readings were nearly constant, and on January 23rd and January 25th no corresponding variations occurred. The eclipse effect was apparently equivalent to a partial return to night conditions.

It is not our purpose to discuss possible explanations of these effects. It seems worth while to point out, however, that the delay in the appearance of an eclipse effect until after the end of totality is not unreasonable, and is in fact to be expected if the effect depends in some way upon changes in the ionic concentration

resulting from changing illumination of the upper atmosphere. A time lag must exist between the beginning of illumination and the attainment of maximum ionic concentration, the duration of which will doubtless be influenced by various atmospheric conditions in a manner that we do not in the least understand. But from the observed persistence of night conditions after sunrise we must conclude that this time lag may have a value as great as an hour or as small as twenty minutes. A lag of the same order of magnitude is therefore to be expected between the end of illumination and the complete disappearance of the ionized condition.

These considerations make it clear that a considerable delay is to be expected between the beginning of the eclipse and the appearance of direction changes, and it is not surprising that the first indication of an eclipse effect is found over an hour after the first contact and just at the close of totality. Night conditions persisted on that day more than an hour after sunrise.

In the path of the eclipse a large reduction is to be expected in the ionic concentration and as we move away from the path of totality, either to the north or south, the ionic concentration increases gradually to its normal value. According to Larmor the velocity is greater in regions of large ionic concentration. A bending of the rays is to be expected, therefore, which will cause them to arrive at Ithaca from a direction south of the true direction of New York.

On the other hand, the explanation of the shift to the north which occurred at 9:40 is by no means obvious. And it is equally difficult to account for the fact that WGY showed no shift to the north such as might reasonably be expected, but merely erratic disturbances. When observations made at other points in the path of the eclipse are available, these difficulties may disappear.

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EXPERIMENTAL LOADING ON GRANULAR MATERIAL.*

BY

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THE engineer, as well as the physicist, is interested in the effects of loading granular material because Nature, over the greater part of the earth's surface, has mantled the rocks with soil, sand, clay, gravel or other granular material. On beds of such material the engineer must frequently found important structures.

The typical granular material, sand, is formed by the breaking down of rock masses. The size and shape of the constituent grains may vary from microscopically small particles such as found in silt, up to titanic boulders, produced and transported by glaciers or mountain torrents. The agency which transported and deposited any particular bed of granular material has also generally segregated the material according to the size, so that we find deposits which we classify as gravel, sand, clay, silt or mud; in any one of which the range in size of grains is small. Sometimes the grains are closely packed, the percentage of void space being nearly a minimum for that particular material; in other beds the grains are loosely packed, and can be consolidated by any influence which promotes a readjustment of the position of grains relative to each other. In beds of fine sand which have been deposited by settlement through water, the grains may even be held apart by the capillary action of entrained water.

The author has found in many cases natural beds of fine supersaturated sand in which the contained water constituted more than half of the total volume. Any increase in the load on such supersaturated sand brings the grains closer together and part of the water which separates the grains is driven off, the reduction in volume being equal to the volume of water driven off. During this process the water exerts hydraulic pressure in all directions,

* Address delivered Wednesday, September 17, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

and the stress distribution in the mass follows approximately the law governing the distribution of stress in liquids.

In dry sand the case is different. The grains are in actual contact. In a horizontally disposed bed, each horizontal layer which now supports all of the superimposed material, may previously, under different geological conditions, have been subjected to much greater vertical load and other influences producing a very compact arrangement.

If the vertical load on a bed of sand is increased the volume may decrease as a result of a rearrangement of the position of individual grains with reference to each other. Sand is slightly compressible. Any increase in load must increase the compression in some direction on each individual grain, and as each grain is an elastic body it is evident that each grain will suffer a slight deformation and a slight reduction in volume. The sum of these volumetric and shape changes will be reflected by a change in the volume of the mass. This volume change is an elastic change and in part at least is recovered on the removal of the load.

Increased loads also cause the crushing of grains, or of the points of contact between grains, and a further reduction in volume results, which change, however, is not recoverable on the removal of the load. Crushing is noticeable in sharp sand at low intensities and increases with the pressure. A stress-strain curve for confined sand shows that for each increment of load the permanent loss of volume increases, while the recoverable elastic change remains nearly constant.

Since the typical sand has little or no cohesion, it can resist only compression, and compression only when lateral displacement is prevented. If lateral motion is absolutely prevented, as when sand is confined in a rigid cylindrical envelope, the effect of equal and opposite forces, acting on the sand in the direction of the axis of the cylinder, is the crushing of grains, the consolidation of the mass and the production of a lateral force exerted against the walls of the cylinder.

The lateral force is caused primarily by the obliquity of the transmission of the direct stress through the sand. If the grains were arranged and maintained in perfect alignment, parallel to the axis of the cylinder, it is possible to conceive that each line would transmit its full proportion of the force, passing from one piston to the other, in which case the lateral force would be that due to

the shape change of the individual grains. But such straight-line paths of force cannot exist in a mass of irregular particles, and the normal path from grain to grain will be oblique to the axis of the force. Since these forces are oblique, they must have horizontal components in addition to the vertical components required to maintain equilibrium. Hence the sum of all the forces acting in a granular material as a result of a vertically applied load must be greater than the load.

The experimental determination of the ratio of the vertical to the horizontal intensity for any given sand is not a simple matter. When sand is confined in a cylindrical container open at the ends, and equal and opposite axial forces are applied to pistons at the ends of the cylinder of sand, the cylinder of sand shortens and exerts lateral force. The friction between the walls of the cylinder and the sand results in an indeterminate part of the axial force leaving the sand and passing through the walls of the cylinder. The pistons themselves probably also act to restrain the sand. So far as the author knows there has been no satisfactory determination of this important ratio.

If the resistance of any grain to lateral motion is less than the lateral component of the oblique force acting on it, then motion will ensue. The direct force transmitted at any point evidently cannot, therefore, exceed that force whose lateral component suffices to cause lateral motion. Lateral motion will occur in that direction in which the ratio of lateral restraint to lateral force is the least and will continue until the restraint increases, or the force is reduced. In general, if there is deficient restraint in any given direction, motion of the sand will ensue until the force finds some other path or paths along which the restraint is sufficient.

Since a granular mass has no cohesion, it can resist only lateral motion by its stability of position, which, for any mass of sand, is due to its weight and the fact that the average grain is supported on points outside of the resultant of the forces which act on that grain.

Bearing these elementary considerations in mind, what then happens when a vertical load is imposed on the upper level surface of a bed of natural sand, through the medium of a platen or footing?

Evidently the horizontal layer of sand immediately below the footing must sustain the entire load. In calculating the stresses

which the footing must sustain, the nearly universal assumption is that the reaction immediately below the footing is uniform over the entire area. Let us assume, for simplicity, a circular footing, and if we represent the intensity of loading by the length of a straight vertical line on any scale, this distribution of load will be represented by that cylinder whose base is the area of the footing and whose height is the length of the line which represents the unit intensity of loading. The volume of this cylinder, being the product of the intensity and the area, will equal the load. It will later appear that this assumption as to distribution cannot be correct.

We know, in general, that below the top of the loaded area the forces acting on the sand are oblique and that, with increasing depth, the area of load distribution increases. We also know the approximate distribution of the vertical components of the load at various levels.

In June, 1917, A. T. Goldbeck published the results of tests he had made on sand. His experiments mark an epoch-making advance in our knowledge of this subject. Using a most ingenious device known as the Goldbeck cell, he measured the vertical components of the pressure acting on a horizontal plane at varying depths in a mass of sand, this pressure being caused by a load applied vertically through loading discs or platens, at the upper surface of the sand. The plane on which measurements were taken formed the bottom of the box or tank containing the sand on which the experiments were made. The amount of load, the size of the platen and the depth of the sand-fill were varied, and the observed intensities plotted for each set of observations.

From his published report I have combined in one diagram the results of a series of tests made by him in which he used a load of 5000 pounds on a circular load platen 13½ inches in diameter (144 inches in area) on sand-fills varying in depth. In this diagram (Fig. 1) I have interpolated the curves (shown by dotted lines) simply to complete the picture. Bearing in mind that the vertical ordinates represent vertical intensities along a diameter passing through the axis of the load, it is evident that the volume obtained by revolving the area contained between the curve and the base of each diagram, being the sum of the products of each unit area by the intensity acting on the area, must equal the volume corresponding to the total load applied.

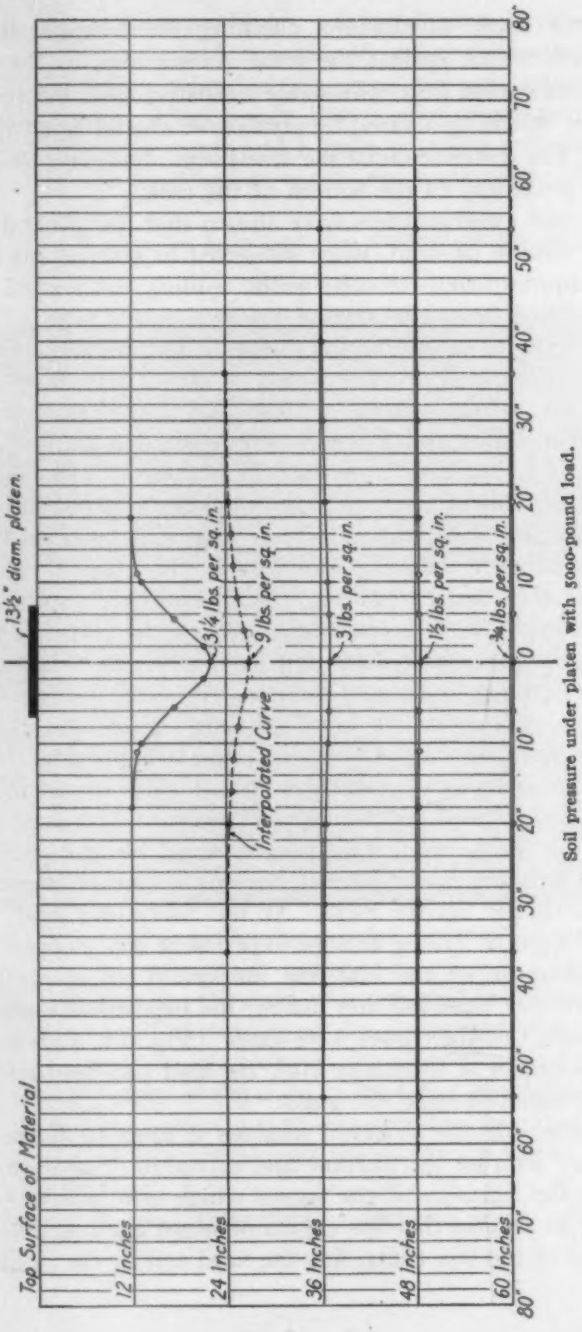

FIG. 1.

Soil pressure under platen with 5000-pound load.

Goldbeck made calculations checking the volume due to the observed curves against the total volume due to the load and found the curves were reasonably consistent with the requirement that the volume generated by each curve should equal the applied load. The distribution of the stress may, however, be influenced by the proximity of the bottom of the tank.

Several experimenters have shown that the general direction of the motion of sand, when subjected to vertical pressure, follows approximately circular paths leading downward, outward and upward from the applied load.

Wishing to determine the direction and amount of the movement of sand, supported on a bed of sand rather than on a solid floor, when acted on by a vertical load, I recently constructed a bin 4 feet square and 3 feet in depth, which was filled with sand placed in layers and compacted by ramming. On this bed of sand, a bottomless box, 2 ft. × 4 ft. in plan, was placed and within this upper box sand was placed in one-inch layers, each layer carefully but lightly tamped. One side of the upper box was made of plate glass braced against lateral pressure.

Where the sand layers abutted against the glass, the planes of separation were marked by thin parting layers of white powder and, at two-inch horizontal intervals, by small pockets filled with the same white material. Finally, a semi-circular platen, 10 inches in diameter, was placed on the sand, the straight side, corresponding to the diameter of a circular platen, being in contact with the plate glass. The platen was then loaded by a lever with gradually increasing loads until 1000 pounds acted on the platen, corresponding to 2000 pounds on a circular platen, or a unit load of 25 pounds per square inch. At the maximum load the glass showed signs of failing and the experiment was stopped. During the application of the load the motion of all points and lines was carefully observed and during the experiments photographs and tracings of the curves were made. Fig. 2 is a photograph of the experiment at this stage after the load had been released and bracing removed from the glass.

In studying the observed motions it must be borne in mind that they indicate the amount and direction of motion, and not directly the intensity of the forces which were acting. It would be rash to assume that the curves obtained are not influenced by the sides of the box containing the sand and by the inequalities in

the compacting of the sand layers. It is believed, however, that they indicate with reasonable accuracy the general direction of the motion of sand when subjected to vertical pressure and also the direction of stress. I am aware that similar experiments have indicated similar movements and I make no claim for originality in the form of the experiment, which was undertaken solely for my own instruction.

In general it may be said that the motion of the platen pro-

FIG. 2.

duced motion and changes in the relative position of the grains of the sand, but unimportant changes in volume. The elastic rebound observed when the load was removed was less than 10 per cent. of the total movement of the platen and was evidently due in large part to the elasticity of the plate glass and probably in part to the elasticity of the sides of the box. No definite planes of shear or sliding were observed except along the upper part of an inverted conical surface beneath the platen, the platen forming the base of the cone.

A study of the movements observed leads to certain conclusions:

(1) The amount of elastic compression and crushing is so small as to be negligible when referred to total movement of the platen.

(2) The sand, immediately below the platen, and inside of a surface which is approximately a 45° inverted cone having the platen as its base, moved downward with the platen. Inside of this conical surface there was only a small vertical movement relative to the platen, such as might have resulted from a slight compression or incipient crushing. The experiment should not be taken as clearly establishing that the shape of the volume or plug under the platen is truly a conical volume. It may be a cone with a rounded or truncated point, or even a hemispherical volume.

(3) All of the sand, exterior to this inverted cone, including the sand vertically below the cone, had a component of motion away from the axis.

(4) All of the sand exterior to the inverted cone had a component of perpendicular motion, which, relative to the glass plate, appeared to be *downward* for all of the sand interior to 45° lines drawn downward and outward from the edge of the platen and *upward* for the sand exterior to the same 45° lines.

As the downward motion of the platen was greater than the downward motion of any part of the sand (except the small volume immediately under the platen) the motion of the sand relative to the platen was consequently *upward*.

From the data at hand it appears that a working hypothesis on which to base further study and experimental measurement would include the following conceptions:

(1) The formation of a plug of sand under the platen having the shape of an inverted cone or something between a cone and a sphere, which plug moves with the platen and changes in volume and shape only as a result of elastic compression, the compacting or crushing of grains within this plug.

(2) The development of stresses on the surface of this plug, the vertical components of which must equal the total load, while the horizontal components cannot exceed at any level the intensity necessary to displace the sand exterior to the plug.

(3) The intensity of upward stress in the material exterior to the platen must reduce to zero at the surface.

(4) The intensity of stress under the platen must have verti-

cal components which increase from the edge to a maximum at the centre.

We may visualize the force applied to the platen, as diverging through the plug, constantly changing direction so that on arrival at the surface of the plug the direction of the forces are normal or nearly normal to that surface. We know that at the surface of the plug the diagonal forces have vertical components, the sum of which equals the applied load. We may consider the sand in the plug as confined. We may conceive of the mass of sand external to the plug as being in compression between the outer surface of the plug and any plane we choose to take outside of the plug. Under increasing application of force to the platen there will be an increasing tendency of the sand to move from the zone of high intensity of compression near the axis of the force toward a zone of low or zero restraint near the top surface of the sand. We may expect that the movement of the sand will be irregular both as to the direction and amount and that it will vary with the mechanical structure of the sand. The movement may occur entirely in one direction if the platen is not kept level. But under similar conditions of loading, we may expect the general character of the movement to be alike.

There is much room for further experimentation and study.

Finally, I wish to emphasize the point that more information on this subject is of vital importance to all engineers who have to deal with the movements of granular material under varying load, and that a better knowledge of this subject will lead to the more intelligent and economical design of footings and a clearer understanding of what constitutes a safe loading on sands whose general characteristics are known.

Ultra-violet Absorption of Petroleum. F. VLES and MISS M. GEX. (*Comptes Rendus,* Jan. 12, 1925.)—These authors have examined the ultra-violet spectrum of crude petroleum oils and of their products by a spectrophotometric method. In a general sense these bodies show in this limited part of the spectrum five chief absorption zones. These are modified as one product after another is removed and a certain regularity is manifested, though "it is still impossible at this moment to determine with certainty the nature of the constituents to which each of these five characteristic bands is related." G. F. S.

A Simple Electrolytic Method of Measuring Current Frequency. A. P. ROLLET. (*Comptes Rendus*, Dec. 26, 1924.)—Two wires of silver one millimetre in diameter placed in an alkaline solution are the electrodes for an alternating current. While a wire is the anode, it is oxidized and a dark layer of oxide of silver is deposited upon it. This is reduced during the time in which the wire is the cathode. While the current is passing, let the electrolyte flow out through the bottom of the containing vessel, thus exposing the wires gradually. The liquid will leave some portion of the wire while it is blackened with oxide. When the opposite phase of the current comes it cannot reduce the exposed oxide because the latter, being above the liquid, is not traversed by the current. As the electrolyte travels down it leaves behind it alternate dark and bright bands on the silver wires. A dark and a bright band together represent one cycle. The apparatus is calibrated by an alternating current of known frequency. It can be used up to 75 cycles per sec. The construction is quite simple. G. F. S.

Ionization of the Atmosphere. A. GOCKEL. (*Phys. Zeit.*, Dec. 1, 1924.)—This article is largely devoted to an indication of investigations that are needed in order that an explanation of the electrical phenomena of the atmosphere may be given. The daily and the yearly variations of the electrical conductivity of the air have been sufficiently examined to make clear that the warming up of the lower layers of air with the consequent disappearance of mist brings as a result a reduction of the conductivity. The most striking features of the daily variation of conductivity near the earth are the minima that come after sunrise and at sunset and the maximum at 4 o'clock. The number of dust particles in the air has likewise minima at 4 A.M. and in the early afternoon, but in summer the early morning minimum travels back toward midnight while the minimum of conductivity fails to do this. Dust would be expected to affect the conductivity in this way. Particles of dust become attached to ions with resultant neutralization or at least reduction of mobility of the ions and it is by the ions that the current is transported through the air. A more thorough investigation of the mobility of the aggregates formed is needed. A greater need is for information in regard to the existence of daily and yearly periods of the factors that cause ionization. Furthermore, extended measurements of vertical currents in the air should be made. If these are determined by influences cosmic in range their fluctuations should show similarity over large portions of the earth. Such uniformity has not been found by the author. In particular the constancy of the strength of the vertical currents along their vertical extent requires examination.

In this paper generous praise is given to the work of L. A. Bauer. G. F. S.

THERMAL DERIVATIONS OF ENERGY FUNCTIONS.*

BY

P. G. NUTTING, Ph.D.

Consulting Engineer.

QUITE a wide variety of energy functions are readily thrown into a form having a term in common which is very suggestive of interrelationships and of more direct applications of the theory of quanta than many previously employed.

Consider a function F of temperature T and other parameters and constants. The mathematical process involved is simply to form the ratio of the logarithmic derivatives of F and T, namely, $dF/F : dT/T$, a ratio of dimensionless quantities, hence independent of any units that may be employed.

In general

$$\frac{dF/F}{dT/T} = f\left(\frac{B}{T}\right) \tag{1}$$

of which the second member $f(B/T)$ is the centre of interest. Consider, for example, van't Hoff's equation commonly written

$$\frac{d(\log K)}{dT} = \frac{q}{RT^2} \text{ or } \frac{dK/K}{dT/T} = \frac{q}{RT} \tag{2}$$

in which $f(B/T) = q/RT$, q being the molecular heat of reaction and K the equilibrium constant of some reversible reaction. As is well known, (2) holds very well for such a wide variety of functions as vaporization, solution, sublimation, chemical combination, dissociation and precipitation.

The radiation ("black body") functions of Wien and Planck take the form

$$\begin{aligned} \frac{dE_\lambda/E_\lambda}{dT/T} &= \frac{c_2}{\lambda T} \text{ (Wien)} \\ &= \frac{\beta\nu}{T} / \left(1 - e^{-\beta\nu/T}\right) = \frac{xe^x}{e^x - 1}, x = \frac{\beta\nu}{T} \text{ (Planck)} \end{aligned} \tag{3}$$

In the simple case of Stefan's law, $E = T^4$, which is the wavelength integral of the above,

$$\frac{dE/E}{dT/T} = 4 \tag{4}$$

a pure number.

* Communicated by the Author.

The rate of diffusion of both hydrogen and carbon dioxide through mild steel has been found proportional to the tenth power of the absolute temperature. In this case

$$\frac{dD/D}{dT/T} = 10 \tag{5}$$

again a pure number.

The Richardson formulas for the thermionic emission of hot metals may be written in the form

$$\frac{di/i}{dT/T} = n - \frac{b}{T} \tag{6}$$

in which $n = \frac{1}{2}$ or 2 and b is the work function, the energy necessary to extricate an electron from a surface at a temperature T. This is in form a combination of (3) and (5) as would be anticipated from physical considerations.

Of the scores of formulas proposed to represent vapor pressure as a function of temperature the majority, when put into the form of (1), fall into one of the three following:

$$\frac{dP/P}{dT/T} = \frac{b}{T}, \; a + \frac{b}{T}, \; a + \frac{b}{T} + \frac{c}{T^2} \tag{7}$$

J. W. Richards' formula for the vapor pressures of the metals is typical of the first ($f(B/T) = b/T$), the second is somewhat more general, the third is equivalent to a formula of Rankine's for the vapor pressure of water over a wide range of temperatures.

In this connection it may be well to point out a simple interpretation of the thermal derivative $dF/F : dT/T$ in (1). If, in plotting any function, say vapor pressure, against temperature, we plot $1/P$ as ordinates against $1/T$ as abscissas on double log paper (or plot log $(1/P)$ against log $(1/T)$ on ordinary paper), then the slope of such curves is nothing more nor less than this thermal derivative. Norton has thus plotted the reduced vapor pressures of a great number of substances against reduced temperatures. In a majority of cases he finds definite, commensurable discontinuities in the slopes. This in our interpretation by (1) signifies merely quantized vapor pressure, or, in other words, stepwise association and dissociation of the vapor.

Forming the thermal derivative of any energy function is a simple means of segregating and throwing into prominence the essential energy relation involved. In every case thus far studied, the second number is either $\beta\nu/T$ or some function of that ratio.

This suggests that all such functions rest ultimately upon quantum relations, the small steps involved being in most cases more or less smoothed out by added constants, factors which are sums of energy conditions out of phase or by the quantum nature of temperature itself.

For example, consider Nernst's expression

$$U = \frac{3}{2} RT \cdot \frac{1}{2} x \cdot \frac{e^x + 1}{e^x - 1} \qquad \begin{matrix} x \equiv \beta\nu/T \\ \beta \equiv hN_0/R \end{matrix}$$

for the energy U, per mol of a substance. In this case

$$\frac{dU/U}{dT/T} = \frac{2x\,e^x}{e^{2x}-1} = \frac{x}{\text{Sinh } x} \tag{8}$$

of which the second member is unity for $x \equiv 0$, and decreases only slowly until x becomes large (*i.e.*, low temperatures and large specific volumes). For the total energy W of a gram-atom

$$W = 3R \frac{\beta\nu}{e^{\beta\nu/T} - 1} \cdot \frac{dW/W}{dT/T} = \frac{x\,e^x}{e^x - 1} \cdot x \equiv \frac{\beta\nu}{T} = \frac{h\nu N_0}{RT} \tag{9}$$

identical in form with (3) derived from Planck's law of radiation. This agreement involves the assumption that radiation of any specific wave-length is proportional to the internal energy of any substance. From (9) the thermal derivative of atomic heat $C = dW : dT$ is readily derived

$$\frac{dC/C}{dT/T} = -2 - x + \frac{2x\,e^x}{e^x - 1}$$

a form suggestive of some empirical generalizations of van't Hoff's equation.

The thermal derivatives of the Einstein and Nernst-Lindemann expressions for specific heat naturally reduce to forms similar to (8) and (9), since all are derived from similar quantum assumptions.

It may be noted in passing that the thermal derivative of thermal conductivity is ½ while for electrical conductivity it is $-½$. In each case modern theory adds a correction factor approaching unity as in (8) and (9).

The general energy-temperature relation usually written

$$A - U = T\,dA/dT$$

if put in the form

$$\frac{dA/(A - U)}{dT/T} = 1 \tag{10}$$

is suggestive of (8) but is not in the form of a thermal derivative as defined by (1). To my mind (10) is to be regarded rather as a definition of temperature than as a fundamental law.

Thus far we have considered only simple forms of $f(B/T)$ in (1). If the reaction equation (2) is to be broadened to cover equilibria over wide ranges of temperature obviously less simple but more exact functions must be investigated. It is quite obvious that if the most general form of $f(B/T)$ consistent with physical and chemical laws is to be determined, an additional criterion will be required. Nernst's so-called third law does not appear to fill this need.

Again, besides the thermal derivative discussed above, two and but two additional general derivatives of similar nature are consistent and applicable in solving problems in general thermodynamics. One of these evidently relates to such quantities as density and external work (possibly in the nature of a generalized Clapeyron equation), the other to structure and chemical potential, the well-known equations between pressure, volume and temperature are far too restricted to be of broad application.

α-ray Tracks in a Strong Magnetic Field. P. L. KAPITZA. (*Proc. Roy. Soc.*, A 739.)—When an α-particle travels through a gas supersaturated with water vapor, its path is made visible by the water condensed upon the nuclei provided by collision of the particle with atoms of the gas. Such tracks have been studied by C. T. R. Wilson and others. Throughout the main part of their length they are straight. In a strong magnetic field, however, a curved path should be followed, because the positively charged particle in motion is equivalent to an electric current and is deflected by the field. The author has devised a plan of getting very strong fields. It is true that they last only about .01 second, but this is a long time in comparison with the ten-millionth of a second required for the completion of the journey of the α-particle.

A description is given of the expansion chamber, mounted in the strong magnetic field, with an arrangement for admitting the particles from polonium for from .001 to .002 second and just .001 second before the end of the expansion by which the gas was made to deposit its vapor on the nuclei. Photographs of the tracks show them to be curved. In hydrogen the curvature is greater than in air, while without a field, the tracks are straighter in this gas than in air. In general "the curvature of an α-particle has a maximum somewhere near the end of its range."

With a small expansion chamber it was possible to get a magnetic field of 80,000 gausses. G. F. S.

THE EFFECT OF BRIGHTNESS ON THE PRECISION OF VISUALLY CONTROLLED OPERATIONS.*

BY

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WITHIN recent years attention has been directed to the rapidity with which operations involving vision can be accomplished under various intensities of illumination. The problem has been approached by psychologists,[1] and by engineers [2] and others, and the results show conclusively that, with all other factors constant, the "output" increases as the brightness or intensity of illumination is increased. The increase in production with the use of higher intensities is considered to result from the fact that visual tasks are made easier and not from any "driving effect" of the bright light. Stated in another way, the ratio of useful work to ineffectual work is increased by the better illumination, and the total energy expended need not be increased. In many operations, the accuracy with which a piece of work can be done is of more importance than the speed, and the advantages of better lighting can be realized in precision rather than in time saved.

In choosing an experimental means of investigating the relation of *brightness* to *precision,* there are many methods and test-objects possible. The ideal arrangement would be such that the time required for vision predominated over that required to manually operate the testing apparatus, and also of such a nature that the experimental results could be applied directly to actual practice. The test-object chosen consisted of two pointed metal strips seen in silhouette against a flat white field as illustrated in Fig. 1. The upper of these was fixed in the centre line of a rectangular opening and the lower one attached to a horizontally sliding rod which could be moved horizontally by rotating a small hand-wheel. This arrangement is also shown in Fig. 1. The task, then, was to set the lower index directly below the upper one within a fixed time allotted to the operation.

* Communicated by the Director of the Laboratory.

In order to realize the full advantage of better lighting in *precision* and not in *speed,* a definite amount of time was allowed for each adjustment of the apparatus, and the observer instructed to utilize *all* of the time given for the operation. By trial it was found, for the conditions of this experiment, that a period of two seconds was sufficient for making a reasonably accurate setting at the lowest brightness used.

Procedure of Test.—The observer was seated at a distance of ten feet from the test-object and in a separate room from the

Fig. 1.

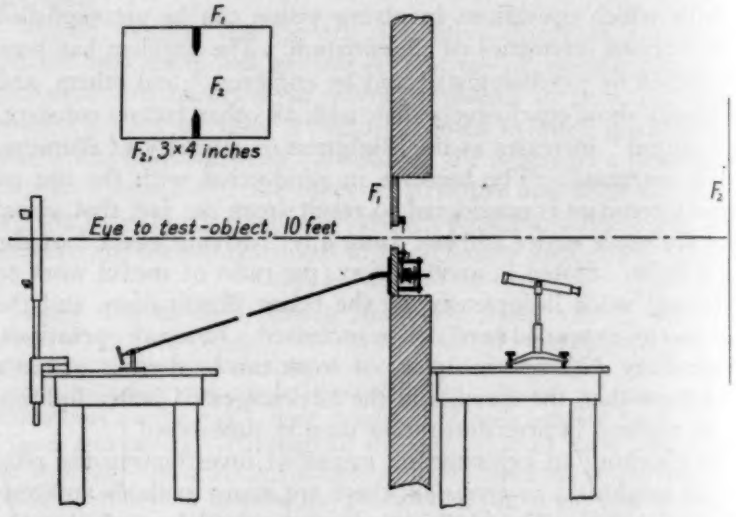


Diagram of the apparatus.

experimenter, and instructed to set the indices opposite each other to the best of his ability within the time given for the operation. The observer was free to establish any criterion that suited him for determining when the indices were in line. Simultaneously with an audible signal a magnetic clutch connected the hand-wheel with the movable index and also released a pendulum with a period of two seconds, which disconnected the hand-wheel from the movable index at the end of that time. The index could not thereafter be moved by the subject and its position was read through a telescope on a scale located below the test-object. The readings were taken in rapid succession with an interval between them of not more than one second.

The ratio of the brightness of the field surrounding the test-object to the background was known to be an appreciable factor in work involving certain visual criteria and was therefore considered in this investigation. For each of the four intensities of background, two sets of data were taken; one with the surrounding field in darkness and the other with the surrounding field illuminated to the same brightness as the background. The color match between the two fields (F_1 and F_2) was made as close as was practicable. Table I is a schedule of the test as performed;

TABLE I.

Diagram Showing the Order in Which the Various Intensities and Field Conditions Were Presented throughout the Test.

Test No.	Field.															
	Dark Surroundings.								Light Surroundings.							
	Brightness, ml.*								Brightness, ml.*							
1	100	5	5	100	100	5	5	100	100	5	5	100	100	5	5	100
2	5	100	100	5	5	100	100	5	5	100	100	5	5	100	100	5
3	20	1	1	20	20	1	1	20	20	1	1	20	20	1	1	20
4	1	20	20	1	1	20	20	1	1	20	20	1	1	20	20	1
5	1	20	20	1	1	20	20	1	1	20	20	1	1	20	20	1
6	20	1	1	20	20	1	1	20	20	1	1	20	20	1	1	20
7	5	100	100	5	5	100	100	5	5	100	100	5	5	100	100	5
8	100	5	5	100	100	5	5	100	100		5	100	100	5	5	100

*The brightnesses are given in approximate numbers for simplicity. One millilambert (ml.) is the brightness of a perfectly diffusing surface having an 80 per cent. reflection factor and an illumination of 1.16 foot-candles.

each figure in the above diagram representing twenty settings for that value of brightness, giving a total of 320 readings for any one day per observer, or a total of 25,600 for the entire test.

Data were taken on ten different observers on eight different days. The observers were fairly representative on a basis of visual acuity.

Results.—The results of the experiment, as read from the position of the movable index on the scale, were examined from the standpoint of consistency (precision of setting) by solving for the *mean variation from the mean setting* for each observer and for each condition of brightness and background.

No effort was made to find a possible correlation of the deviation between the *mean of the settings* and the correct physical alignment of the indices. In actual practice, such as the lowering of a rotating drill over a punch-mark, for example, the worker

would have a criterion of his accuracy and after a few trials proper correction could be made for any discrepancy other than simple lack or precision. In the experiment, the observer had no means of knowing the results of the previous adjustment so that deviations from the geometrically exact position would have little significance.

The results of the tests are summarized in Table II. Each value given in the table is the mean variation in centimetres obtained from 320 readings taken under the specified conditions.

TABLE II.

Individual and Average Mean Variations Obtained for the Several Conditions of the Test.

Observer Number.	Dark Surroundings. Brightness, ml.				Light Surroundings. Brightness, ml.			
	1.00	4.18	20.00	91.50	1.00	4.18	20.00	91.50
1	.0840	.0679	.0561	.0630	.0501	.0622	.0512	.0463
2	.0829	.0658	.0715	.0629	.0794	.0656	.0786	.0594
3	.0531	.0519	.0511	.0517	.0556	.0488	.0475	.0453
4	.0844	.0741	.0754	.0716	.0704	.0669	.0693	.0606
5	.0966	.0864	.0783	.0736	.0856	.0745	.0764	.0681
6	.0561	.0597	.0502	.0528	.0553	.0529	.0448	.0458
7	.0579	.0534	.0523	.0509	.0556	.0521	.0500	.0488
8	.0918	.0825	.0722	.0706	.0796	.0678	.0690	.0659
9	.0813	.0864	.0613	.0793	.0664	.0676	.0539	.0591
10	.0579	.0617	.0501	.0488	.0513	.0584	.0438	.0530
Average	0.0745	.0690	.0618	.0625	.0649	.0619	.0584	.0552

* Figures in table are the average of four tests having the same brightness and background.

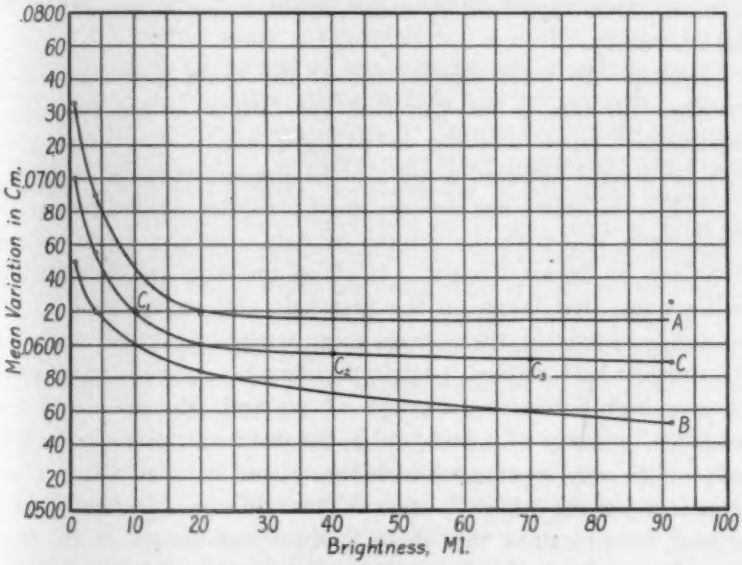
The average results given by ten observers are shown plotted in Fig. 2. The curves *A* and *B* show the relation between *brightness* and *mean variation* for the dark and light surroundings, respectively. Curve *C* is an average of the two curves *A* and *B* and would, in all probability, approximate the relation between brightness and mean variation in practice where the two fields, F_1 and F_2, are seldom balanced for intensity and color.

The curve is asymptotic to certain values of both brightness and mean variation. Actually, there is a limit along the axis of mean variation since the factor of "touch" or the ability to set the apparatus within certain limits of precision relying but little on vision, enters and predominates at threshold values of brightness. Again, the asymptotic character of the curve would be

altered at extremely high values of brightness due to the factor of glare. As the width of the indices subtends an angle of 5.7 minutes at the eye and is therefore well above the critical angle for visual acuity, the gain in accuracy will reach a practical limit which may be placed approximately at 20 millilamberts.

From the relation found between brightness and mean variation it is reasonable to assume that with test-objects of other

FIG. 2.



Curves *B* and *A* give the relation between brightness and the mean variation of the settings for light and for dark surroundings, respectively. Curve *C* is the average of curves *A* and *B*; points C_1, C_3 and C_2 were obtained by interpolation.

physical dimensions, a similar relation, mean variation as a function of brightness, would result.

The probable error for any one of the points plotted in Fig. 2 is small enough to make the above conclusions significant:

$$E = \frac{0.6745 \times M.V.}{\sqrt{2 \times 3200}} = 0.0084 \times M.V.$$

Where E = the probable error; $M.V.$ = mean variation and 3200 is the number of readings involved.

The results of this investigation can be applied directly to many industrial operations. In cases where the output is on a quantity-production basis, with the various operations following

one another at fixed and predetermined intervals, the conditions encountered parallel those of the test and *the gain in accuracy found in the laboratory could be expected in practice.*

Illumination and Eye Fatigue.—The evidence that higher intensities enable a worker to produce more work, or the same work with better precision, has given rise to the conclusion that the worker has been induced to function at an unnatural rate and consequently would be more fatigued at the end of the day. This opinion is not supported by observations either in practice or in the laboratory.

Perhaps the most simple, and at the same time conclusive, evidence for this is the fact that eye fatigue is not commonly experienced when working in daylight where the illumination may be several hundred times that of present artificial lighting.[3]

While the above test was designed for other purposes than for eye fatigue, still with the volume of data obtained, some conclusions can be drawn from it. If all of the data are divided into two groups, that taken on the first half and second half of the session, respectively, the average mean variation is 7 per cent. less for the first half session. Again dividing the data into groups of relative high intensity (average of 20 and 100 ml.) and low intensity (average of 1 and 5 ml.), the mean variation on the first half of the day, compared with the second half, is about 1 per cent. less for the "high" value. This difference is small, but it at least fails to show that there is any disadvantage in the high intensity on the basis of eye fatigue, and it might even be construed to favor the latter.

The authors wish to acknowledge their indebtedness to M. Luckiesh for suggesting this line of work; and to other members of the Lighting Research Laboratory and also various other employees at Nela Park for their assistance in acting as subjects.

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THE EFFECT OF MOISTURE AND TEMPERATURE ON THE POWER FACTOR OF TRANSFORMER OIL.*

BY

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IT IS quite obvious that when the effects of various treatments of a particular sample of transformer oil are to be studied, the test itself should not materially change the characteristics or destroy the sample under consideration. For this reason in this investigation of the effects of temperature and moisture on transformer oil the dielectric strength test was not chosen. In the dielectric strength test the passage of the arc carbonizes an appreciable amount of oil. Moisture and other impurities are drawn into the strong field between the electrodes so that these impurities are altered or removed by the electric discharge. Hence, after the first puncture test, it is impossible to say that successive tests upon the same sample really mean anything with regard to the original sample. Furthermore, one finds, if a fresh sample is taken for each determination, that a great amount of time is consumed and even this is attended by great disappointment in the wide range of values that are obtained.

A test for dielectric losses and power factor is more free from the objections to which the dielectric strength test is subject. This test may be applied over a range of voltage up to the neighborhood of breakdown without materially changing the sample. Continuous tests may also be made on the same specimen under varying conditions. The greatest objection to this method of test is the fact that quite sensitive instruments are required, since the losses and power factor of a good transformer oil are quite small.

There are four methods commonly employed in making dielectric loss measurements, namely, (1) the electrostatic wattmeter method, (2) the Wien bridge method, (3) the cathode-ray wattmeter method, and (4) the electrodynamometer wattmeter method. The first of these methods has distinct advantage. It can be made very sensitive so that very small losses may be

* Communicated by the Author. The work on which this article is based was done at the Research Laboratory of the Westinghouse Electric and Manufacturing Company at East Pittsburgh, Penna.

measured. At any voltage, losses over a large range may be measured and losses may be measured over an extended range of voltage. Because of its adaptability and flexibility in these respects, the use of the electrostatic wattmeter has been adopted by the writer for the measurements of losses upon which power factor determinations are made.

The electrostatic wattmeter was first used by Potier. Its use has been highly developed at the National Physical Laboratory, London. It has been extensively used by Walker,[1] Rayner,[2] and Skinner,[3] for dielectric measurements.

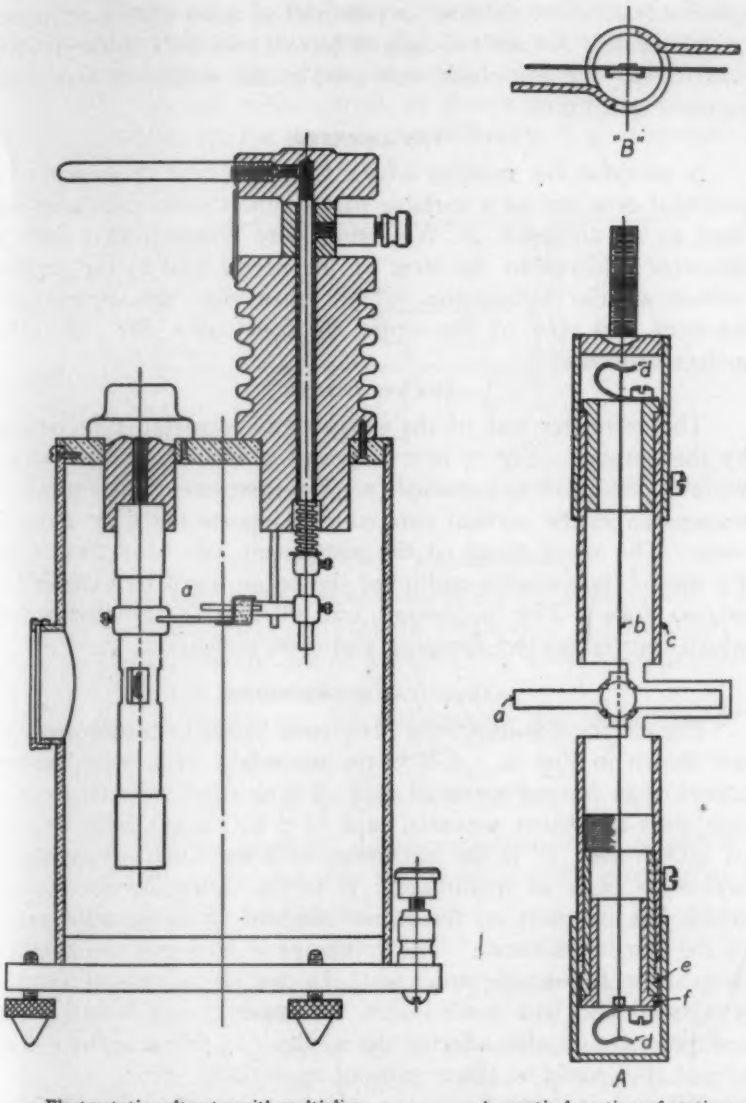
The instruments for the measurement of power factor by the electrostatic wattmeter method include: (1) A Kelvin electrometer used as a wattmeter, (2) an electrometer of the Compton type adopted for use as an ammeter, (3) a non-inductive high resistance to be used as a shunt across the quadrants of the Kelvin electrometer, and (4) an electrostatic voltmeter for indicating applied potentials.

THE WATTMETER.

The quadrants of the Kelvin electrometer were five inches in diameter. The quadrant chambers were one inch high and the space between quadrants was about one-eighth inch. The opening through the axis of the quadrants through which the stem of the needle passed was one inch in diameter. The needle made of 0.007-inch sheet aluminum was three inches in diameter and each vane was approximately the quadrant of a circle. The vane of the needle was clamped between the two parts of a brass cylinder one-fourth inch in diameter and five-eighths inch long which were made to screw together. The stem carrying the mirror was fastened to one part of the cylinder and a stem carrying a small mica vane was fastened to the other. The mica vane extended through the quadrants into a small glass cup of transformer oil. By properly adjusting the size of the vane and the cup, the needle was properly damped and was prevented from being pulled against the quadrants in case too large a potential was applied to the needle. The suspension was a single strip of 0.002-inch phosphor-bronze wire about six inches long. The instrument was adjusted by arranging the needle symmetrically with respect to the quad-

[1] WALKER: *Trans. A. I. E. E.*, Vol. 19, 1902, p. 1035.
[2] RAYNER: *Jour. I. E. E.*, Vol. 49, 1912, p. 3.
[3] SKINNER: *Trans. A. I. E. E.*, Vol. 19, 1902, p. 1047.

FIG. 1.



Electrostatic voltmeter with multiplier.

A—vertical section of stationary and movable vanes. *B*—horizontal section of stationary and movable vanes.

rants and levelling the instrument or altering the height of the needle until no deflection of the needle took place when, with the quadrants all short-circuited, a potential of 2000 volts was applied to the needle. A Curtis resistance box of two dials, 1000–10,000, and 10,000–100,000 ohms, was used as the resistance across the pairs of quadrants.

THE AMMETER.

A sensitive electrometer of the Compton type to measure the potential drop across a variable part of the Curtis resistance was used as an ammeter. A Wolloston wire about 0.0003 inch in diameter soldered to the stem of the needle and to the support served as the suspension. The sensitivity was remarkably constant and was of the order of four volts for 200 millimetres deflection.

THE VOLTMETER.

The voltmeter was of the electrostatic repulsion type devised by the author.[4] Fig. 1 is a diagram of the instrument with a variable condenser as a multiplier. The instrument has a torsional suspension in the vertical axis which supports the light movable vane. The lower range of the instrument was 0 to 2000 volts. By use of the variable multiplier the range could be extended to 20,000 volts. The instrument was filled with transformer oil which insured perfect damping and good insulation.

ELECTRICAL CONNECTIONS.

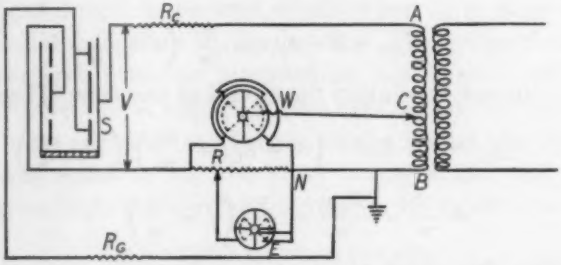
The electrical connections for power losses in transformer oil are shown in Fig. 2. *A-B* is the secondary of a 5-kw. testing transformer having potential taps of 0 to 2000 volts in steps of 200 volts and other potential taps of 0 to 14,000 volts in steps of 2000 volts. *W* is the wattmeter with the Curtis resistance *R* across its pairs of quadrants. *E* is the Compton electrometer which has its pairs of quadrants shunted by a variable part *r* of the Curtis resistance. The voltmeter *V* measures the potential drop across the sample under test. In case the sample to be tested was small and had small losses, the capacity and losses of the voltmeter appreciably affected the results. In this case the voltage across *A-B* could be taken without appreciable error.

When it is desired to make tests at voltages higher than can be put directly on the wattmeter needle, advantage can be taken

[4] SHRADER: *Jour. Opt. Soc.*, April, 1922.

of the method of Miles Walker [5] which provides for charging the needle by potential taps intermediate between A and B. When guard rings are used in the test cup as employed in these experiments, a non-inductive resistance R_G, of such value that the potentials of the guard rings and the central electrode are kept the same, was included in the circuit, as shown in the diagram. To avoid correcting for the losses in the resistance R, a compensating

FIG. 2.



resistance R_C of proper value, as employed by Walker, was inserted as shown.

THEORY OF POWER MEASUREMENT.

The theory of power measurement by the electrostatic wattmeter has been given in various textbooks.[6] The following theory, derived for the use of a guard ring when a compensating resistance is used, is contributed.

From the theory of the electrometer the deflection D is given by,

$$D = K \frac{1}{T} \int_0^T (2V_{MC}d + d^2)\, dt,$$

where V_{MC} is the potential difference between the quadrant M and the needle at C, and d is the potential difference across the pairs of quadrants. (Fig. 2.)

Let

$$n = \frac{V_{AB}}{V_{BC}}, \quad \text{then } V_{AC} = V_{AB}\left(1 - \frac{1}{n}\right)$$

where V_{AB} is the potential across the secondary of the transformer and V_{AC} is the potential from the terminal of the transformer A to the potential C to the needle.

[5] WALKER, MILES: *Loc. cit.*

[6] See Laws' "Electrical Measurements," pp. 320–322.

When the guard ring is employed let

$$m = \frac{\text{total current to the sample}}{\text{current to the central part of the electrode}}.$$

If the charging current for the needle of the wattmeter is negligible, the voltage between the quadrant at M and the needle connected at C is,

$$V_{MC} = V + R_C i - V_{AC} = V + R_C i - V_{AB}\left(1 - \frac{1}{n}\right)$$

But

$$V_{AB} = V + R_C i + \frac{Ri}{m}\left(1 - \frac{1}{n}\right)$$

where i = current flowing in the circuit at any time. Then

$$V_{MC} = V + R_C i - \left(V + R_C i + \frac{Ri}{m}\right)\left(1 - \frac{1}{n}\right)$$

$$= \frac{V}{n} + \frac{R_C i}{n} - \frac{Ri}{m}\left(1 - \frac{1}{n}\right)$$

Substituting this value for V_{MC}, we have,

$$D = K\,\frac{1}{T}\int_0^T \left\{\frac{2Vd}{n} + \frac{2R_C R i^2}{mn} - \frac{2R^2 i^2}{m^2}\left(1 - \frac{1}{n}\right) + d^2\right\} dt$$

Putting

$$d = \frac{Ri}{m}$$

Then,

$$D = K\,\frac{1}{T}\int_0^T \left\{\frac{2Vd}{n} + \frac{2R_C R i^2}{mn} - \frac{2R^2 i^2}{m^2}\left(1 - \frac{1}{n}\right) + \frac{R^2 i^2}{m^2}\right\} dt$$

The term $\frac{2dV}{n}$ is proportional to the instantaneous power. To eliminate the other terms in the equation, set their sum equal to zero and solve for R_C.

$$\frac{2R_C R i^2}{mn} - \frac{2R^2 i^2}{m^2}\left(1 - \frac{1}{n}\right) + \frac{R^2 i^2}{m^2} = 0$$

and

$$R_C = \left(\frac{n-2}{2}\right)\frac{R}{m}$$

When no guard ring is used $m = 1$ and the usual expression for the compensating resistance is obtained.

If R_C is adjusted to this value, then,

$$D = \frac{2KR}{n}\,\frac{1}{T}\int_0^T Vi\,dt = \frac{2KR}{n}\,W$$

where W is the power in the load, or

$$W = \frac{nD}{2KR}$$

If $n = 2$, or if one-half the potential of the whole transformer is applied to the needle, $R_C = 0$ and no compensating resistance is required.

In the above equation the deflection D is proportional to R. This has been found to be true except when R is large and the entire potential is applied to the needle. The proportionality is much nearer true when an intermediate tap is used and only a part of the potential is applied to the needle. A further advantage of using a potential tap for the needle is that the wattmeter may be made sensitive for the lower voltages and still may be used for quite high voltages by increasing the value of n.

CALIBRATION OF INSTRUMENTS.

To determine K the constant of the wattmeter, a known capacity and resistance were inserted in the circuit as the load. With a known voltage, E, the current, I, in the circuit was calculated. The watt loss is given by $EI \cos \theta$. Cos θ was calculated from the values of the capacity and resistance.

Now,

$$K = \frac{nD}{2RW} = \frac{nD}{2R\left(EI\cos\theta + \frac{I^2R}{2}\right)}$$

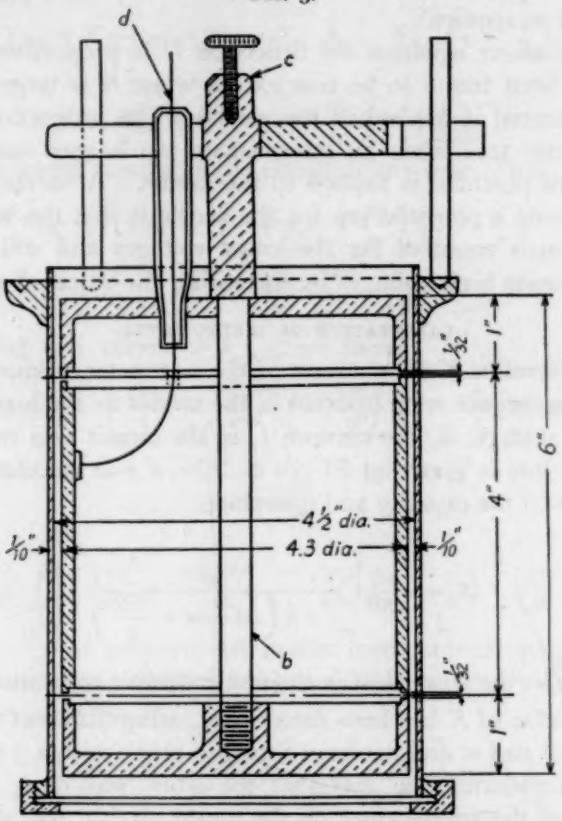
where $\frac{I^2R}{2}$ is the power lost in the non-inductive resistance R.

The value of K has been determined, using different values of E, R, cos θ and n, and has been found to check within 3 per cent., which, considering the fact that the work was done with the primary of the transformer on the power circuit, was extremely good. Tested from day to day, very small deviation from the value of K was observed. The value of K used in most of these experiments was 0.065.

The ammeter, for which the Compton electrometer and a part r of the resistance R were used, was calibrated as follows: With a given voltage and impedance the current in the circuit was calculated. The resistance r was varied and the deflections of the

electrometer were noted. A curve was then plotted, showing the variation of the deflection d with $e = rI$, the voltage drop across the quadrants. Taking the value of e from the curve corresponding to the deflection, the value of $I = \frac{e}{r}$ was obtained.

FIG. 3.



THE OIL TEST CUP.

The form and construction of a test cup for oil is quite important. The form should be such that the electrodes are vertical so that air bubbles are not entrapped and that air and vapors released during heating may readily escape. The construction should be such that the supporting insulation is outside the electric field. To prevent errors due to unavoidable non-

uniformity of electric field, guard rings should be provided. It is believed that the form and construction of the test cup shown in Fig. 3 most nearly meet these requirements. The test cup consisted essentially of two coaxial cylinders of dimensions given in the figure, the inner having a guard ring at either end. The inner cylinder with its guard rings was suspended inside the outer cylinder by three glass rods held by arms attached to the inner cylinder. These glass rods rested in a groove in a rim attached to the outer cylinder. In this way the insulating and supporting rods were entirely outside the electric field. The end effect of the inner cylinder was reduced by closing the bottom of the outer cylinder with mica held in place by a ring, *a*, screwed to the outer cylinder. The guard rings with outer ends closed were separated from the central part of the inner electrode by diaphragms of mica. The whole inner electrode was held together by the threaded rod, *b*, through the axis. The binding post, *c*, makes electrical connection to the guard rings. A wire, *d*, fastened to the central part of the inner cylinder and brought out through the glass rod ground into the upper electrode, served as the second connection to the inner electrode.

The cylinders were adjusted concentrically by holding in place by spacers, while the rods were clamped to fit the groove. The spacers were then removed and no subsequent adjustment was necessary when the parts were placed together.

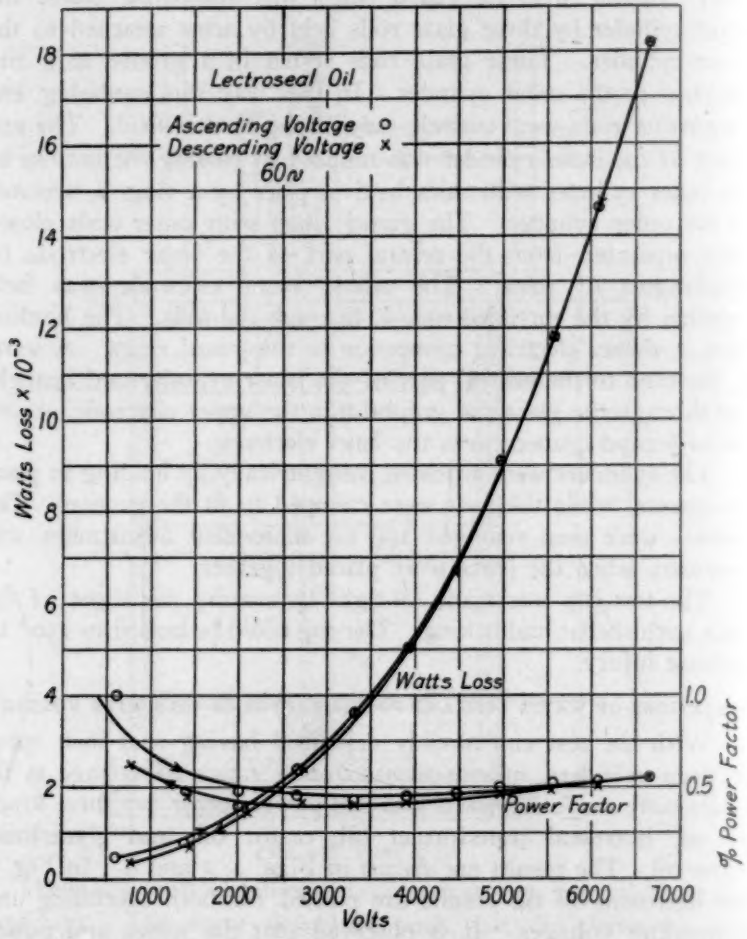
The test cup was made oil-tight by coating the edges of the mica with shellac and baking. The cup could be heated to 150° C. without injury.

VARIATIONS OF WATTS LOSS AND POWER FACTOR OF OILS WITH VOLTAGE.

With the test cup already described having a .1-inch space between cylinders, measurements over a range of voltage at 60 cycles were made for watts loss and power factor for three kinds of oil, lectroseal transformer oil, castor oil, and glycerinum petræ oil. The results are shown in Figs. 4, 5 and 6. In Fig. 4 for lectroseal oil the results are plotted for both ascending and descending voltages. It is observed that the losses and power factor fall slightly with descending voltage. This is no doubt due to the settling out of slight impurities under the electric stress. For all three oils the power factor falls slightly to a minimum, after which there is a slight increase. For lectroseal this mini-

mum occurs at 3500 volts for increasing voltage with a power factor of 0.45 per cent., for castor oil at 6000 volts with a power factor of 0.75 per cent. and for glycerinum petræ at 2000 volts with a power factor of 0.22 per cent.

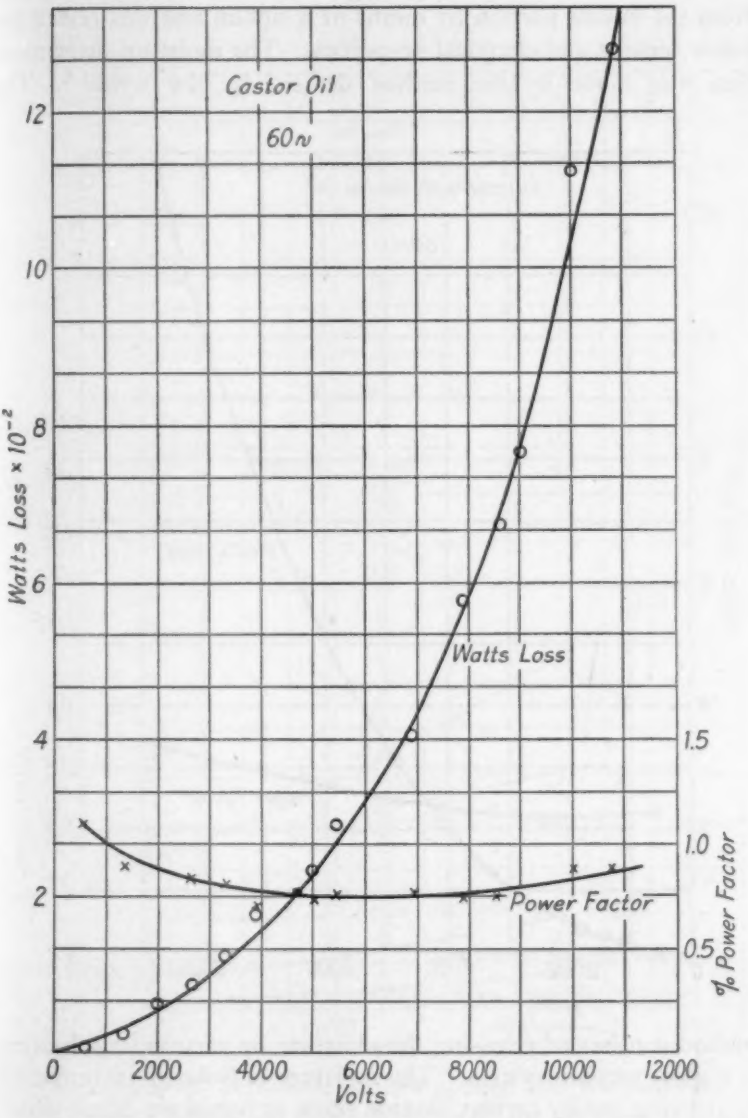
FIG. 4.



THE EFFECT OF MOISTURE ON THE DIELECTRIC LOSS AND POWER FACTOR OF LECTROSEAL TRANSFORMER OIL.

A mixture of oil and water was prepared by stirring equal portions of lectroseal transformer oil and distilled water by

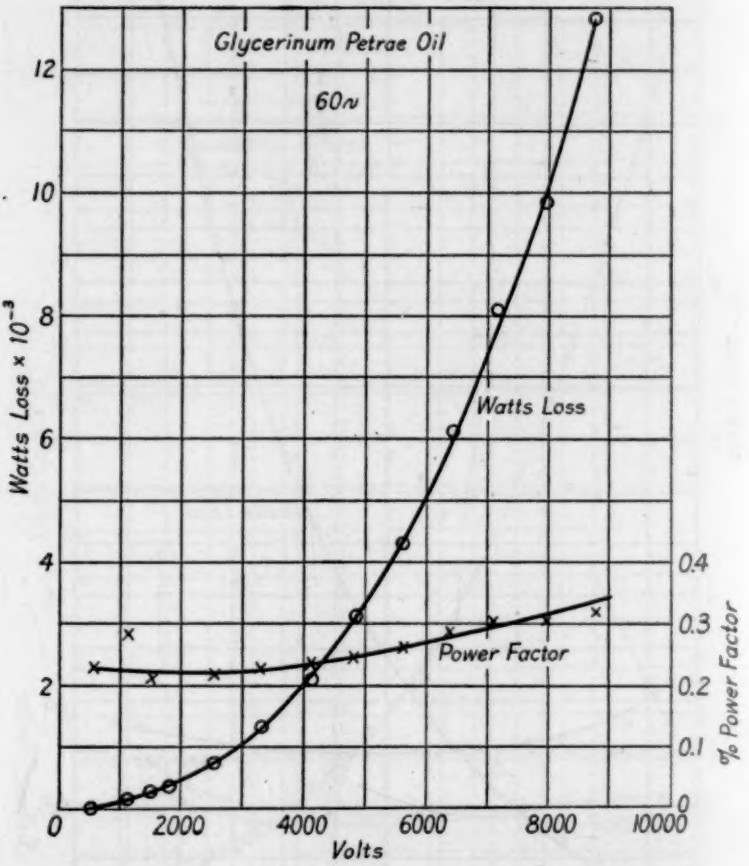
FIG. 5.



motor-driven stirrer for about five hours. At the end of that time the mixture was allowed to stand for one hour, at the end of which time the oil was decanted off into a large bottle and allowed

to stand one hour longer. At that time a sample of oil was taken from the middle portion by means of a siphon and was tested for water content and electrical properties. The moisture determination was made by the method devised by the writer.[1] The

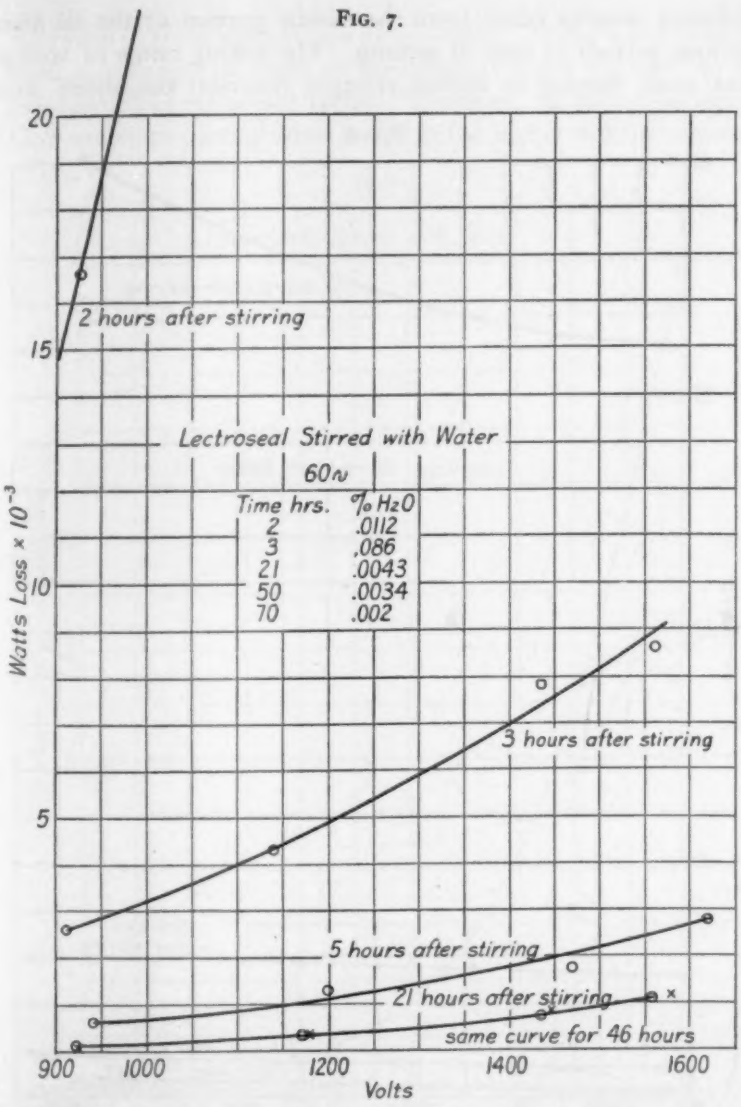
FIG. 6.



method consists of releasing the moisture by vacuum and heating in a glass vacuum system. The moisture is isolated from the oil by freezing out by carbon dioxide snow or liquid air, after which it is permitted to reëxpand and the vapor pressure of the water together with that of the oil is determined. A side tube con-

[1] SHRADER: *Elec. World*, Vol. 79, No. 4, p. 174.

FIG. 7.

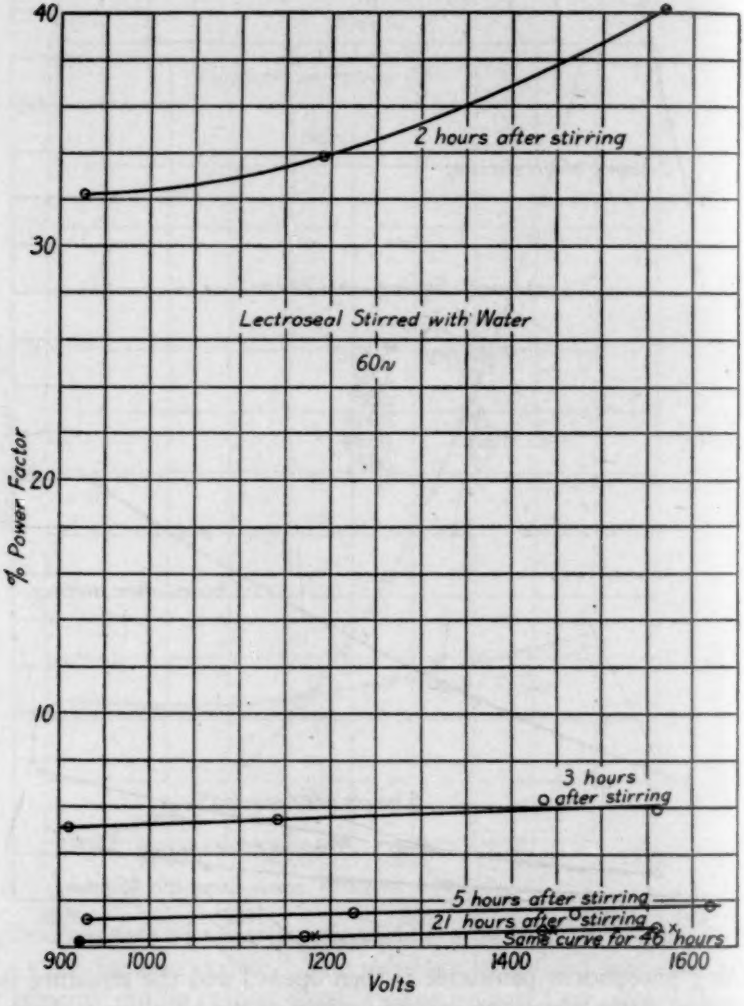


taining phosphorus pentoxide is then opened and the moisture is absorbed, after which the vapor pressure of the oil alone is determined. Thus, the vapor pressure of the water and its volume being known, the moisture content of the oil may be determined.

Fig. 7 shows the variation of watts loss with voltage for

different samples taken from the middle portion of the oil after various periods of time of settling. The testing range of voltage was small because at higher voltages electrical conditions were

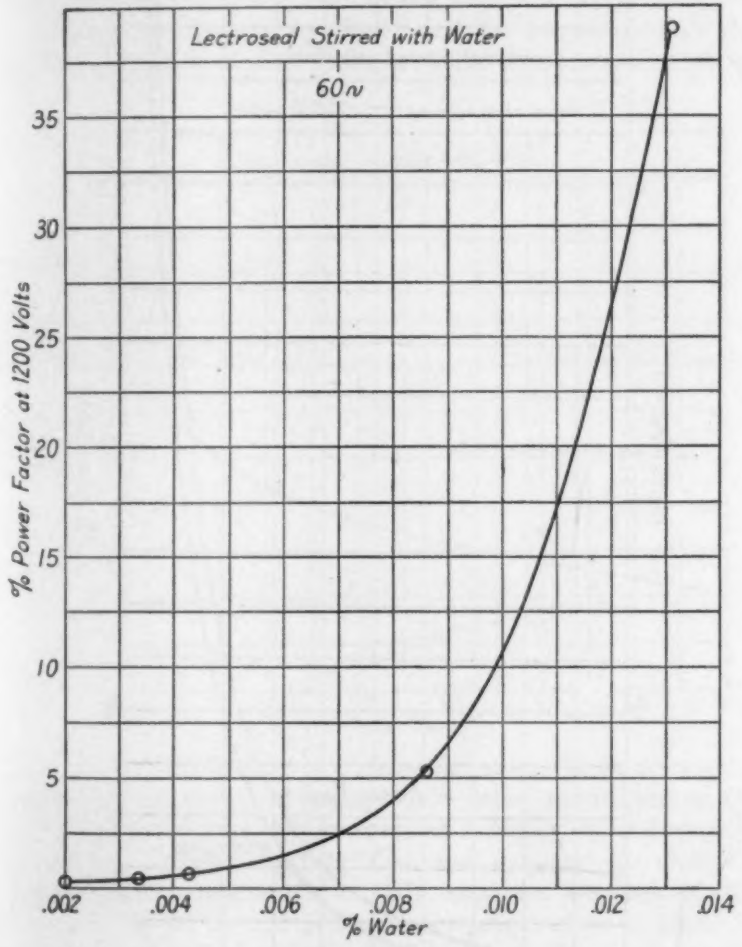
FIG. 8.



unstable, especially for the samples having the higher moisture content. Fig. 8 shows the corresponding changes in power factor with voltage. Fig. 9 shows the variation of power factor at 1200

volts with varying percentages of moisture. At the lower voltages small percentages of water of the order of 0.002 per cent. do not seriously affect the power factor. However, the mixed oil having a low moisture content when tested at the higher voltages shows a

FIG. 9.



very rapid increase of power factor with voltage. This is shown in Fig. 10. This is in sharp contrast with the results for lectroseal oil shown in Fig. 4, which had not been mixed with water, but which had approximately the same water content.

FIG. 10.

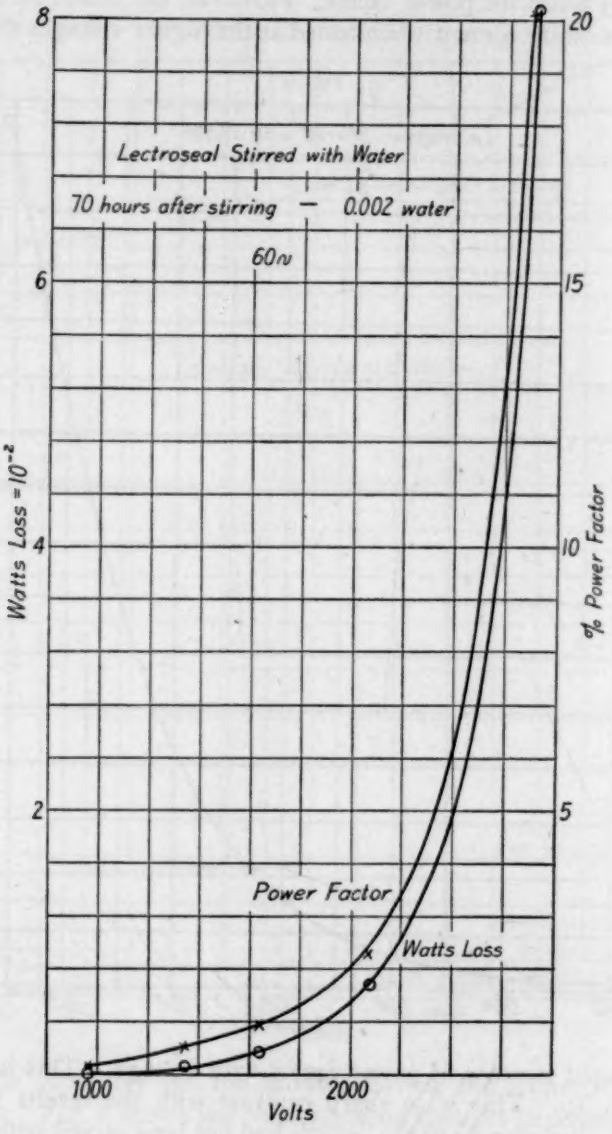
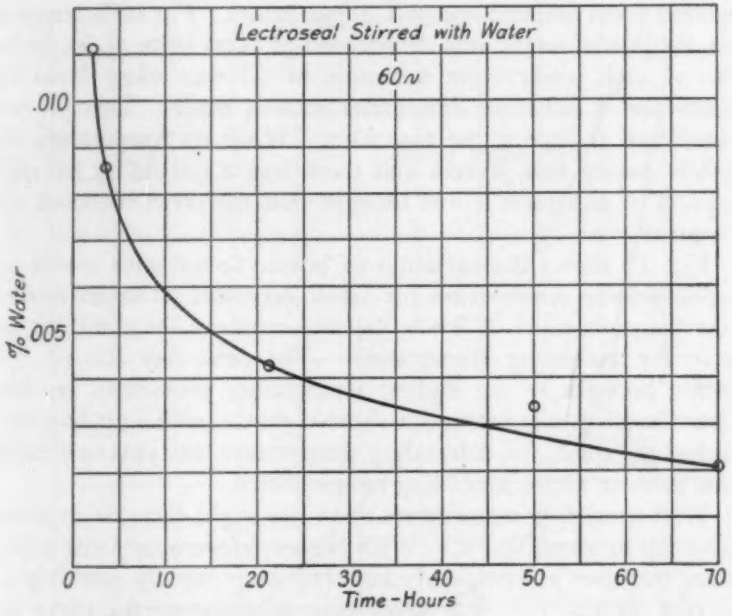

Lectroseal Stirred with Water
70 hours after stirring — 0.002 water
60∿
Watts Loss = 10^{-2}
% Power Factor
Power Factor
Watts Loss
Volts
1000
2000
8
6
4
2
20
15
10
5

Fig. 11 shows how rapidly mechanically mixed oil and water separate. The rate is very rapid at first, but becomes slower and slower with time. After three or four days the moisture content for the middle portion of the containing vessel is about the same as for the original oil.

EFFECT OF TEMPERATURE ON THE POWER FACTOR OF LECTROSEAL OIL.

It has been observed by Peek[8] that for transformer oil the dielectric strength at first increases with temperature to about

FIG. 11.



75° C., after which there is a slight decrease. With descending temperature the dielectric strength falls below the maximum for ascending temperature, but remains at a higher value for room temperature. Peek suggests that the increase of dielectric strength with temperature is only apparent because of the increased flow of current at the higher temperature or else it is due to the removal of moisture with heating. For further study of the effect of heating transformer oil, measurements of power factor and moisture determinations were made under identical

[8] PEEK: "Dielectric Phenomena in High Voltage," *Engineering*, p. 155.

conditions of treatment. The test cup already described was filled with the sample of oil and placed inside an electrically heated, thermostatically controlled oven. Alongside the test cup was placed in a beaker a sample of the same oil upon which water determinations were to be made. Leads were brought into the oven to the test cup so that the electrical measurements could be made at any desired temperatures. For each temperature the oven was brought up to temperature as quickly as possible and maintained at that temperature until the electrical measurements showed that equilibrium had been established. This usually required from one and one-half to two hours. For each temperature the power factor was determined at 7000 volts at 60 cycles. Also at each temperature a sample of oil was taken from the beaker and a moisture determination was made. This oil was transferred at once to the apparatus. While its temperature fell slightly during this process and there was a possibility of reabsorption of moisture, it was thought that the error involved was not great.

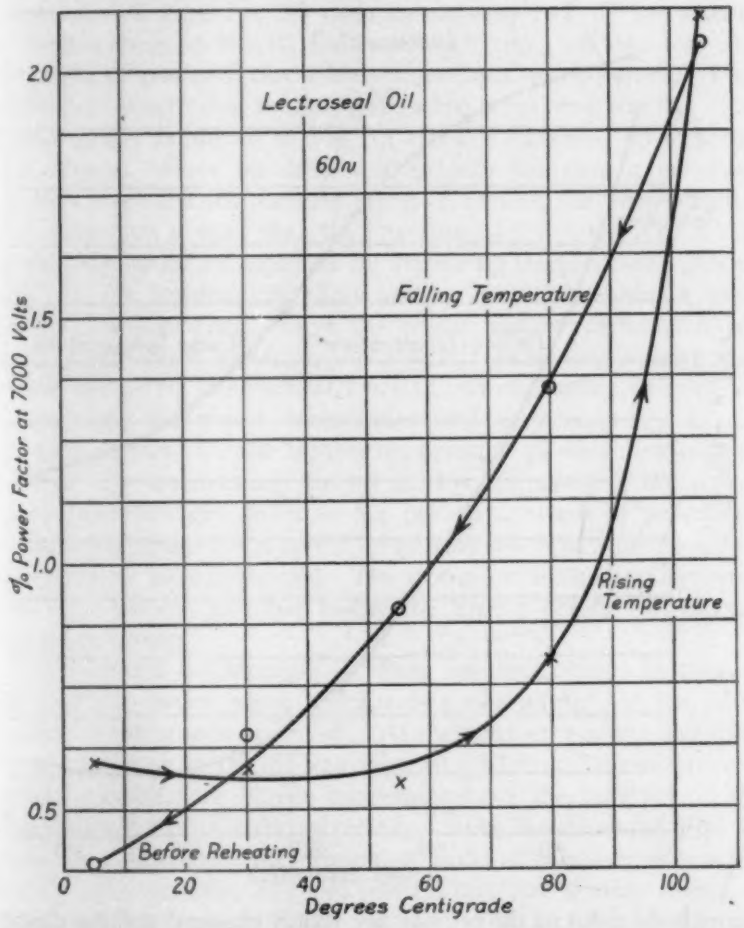
Fig. 12 shows the variation of power factor with increasing and decreasing temperature for fresh lectroseal oil taken directly from the stock can. A whole day was required for obtaining the curve for ascending temperature. The next day the oil was quickly brought to the highest temperature previously reached. After electrical measurements showed that equilibrium had been reached the curve for descending temperature was obtained in the same manner as for ascending temperatures.

With ascending temperature there is a slight decrease in power factor up to about 60° C. With higher temperatures the power factor increases at first slowly and then more rapidly reaching 2.1 per cent. at 125° C. For descending temperature the curve lies above that for ascending temperatures down to 47° C., below which the power factor is smaller than for ascending temperature. These results are analogous to Peek's results on dielectric strength measurements.

The curves of Fig. 13 show how the water content varies for ascending and descending temperature under the same conditions under which the power factor had been determined. With rising temperature, water is continuously being driven off. The water content has been reduced from 0.0023 per cent. at 25° C. to 0.0013 per cent. at 0.125° C. After reheating, the water content

has been further reduced to 0.00075 per cent. at 125° C. With descending temperature, moisture from the air is again reabsorbed so that nearly the original amount of moisture is found when 25° C. is reached. It is no doubt true that these results are

FIG. 12.

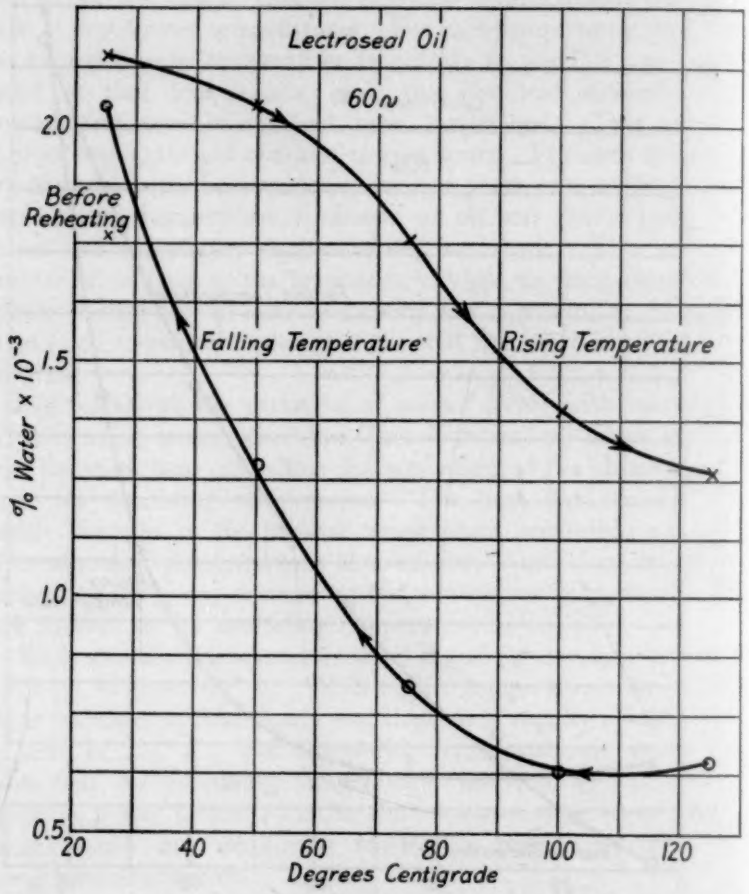


affected somewhat by the humidity of the atmosphere on the two different days and it is regretted that no humidity determinations were made.

The fact that there is a decreased absorption of moisture at the higher temperature for the reheated oil, would suggest that

the oil had undergone some chemical change such that its water solubility was different at the higher temperature. By heating at 125° C. some of the lighter constituents would be driven off. Likewise heating in the open air would result in slight oxidation,

FIG. 13.



though the color of the oil was not visibly changed and the change in the electrical properties was not marked.

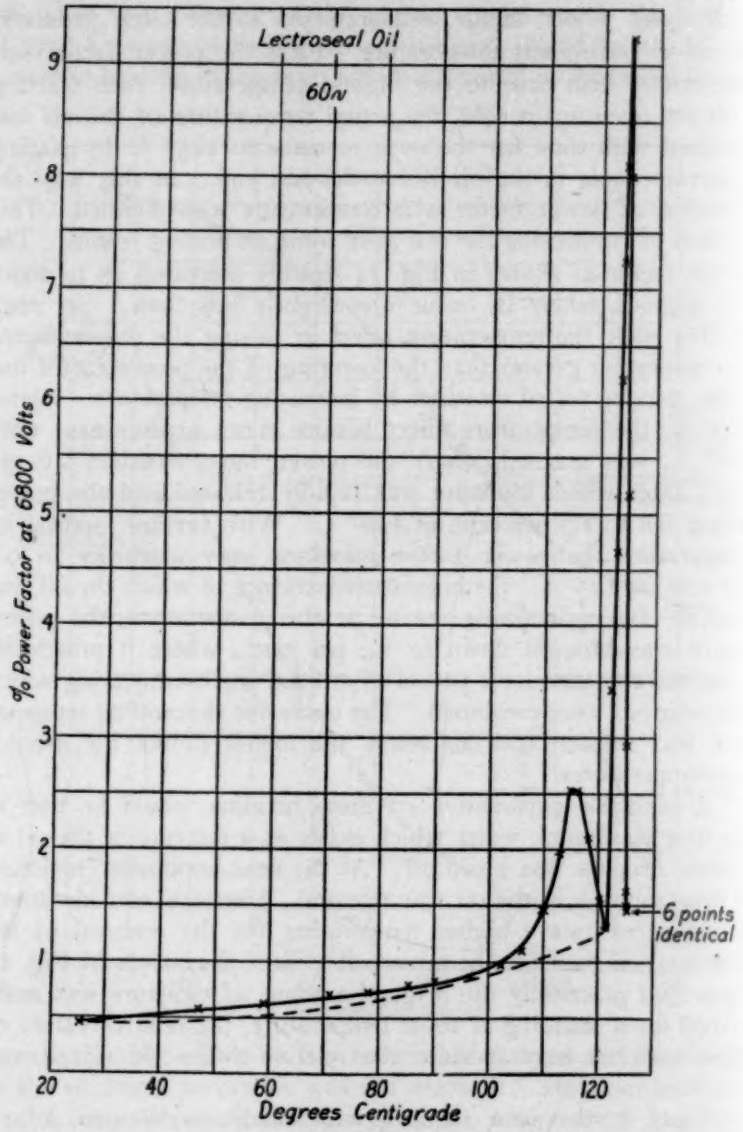
In the experiment just described the temperature had been kept constant until equilibrium had been established and from these results the curves had been plotted. A variation of power factor with temperature for continuous heating up to 125° C.

was obtained by placing the oil in the oven at room temperature and taking power factor measurements as the oven gradually heated to its highest temperature. First the power factor was determined with time to the highest temperature, then starting with the oven again cold, the actual temperature of the oil was obtained with time for the oven to come to 125° C. by placing a thermocouple in the oil inside the test cup. In this way the variation of power factor with temperature was obtained. This method of conducting the test gave some surprising results. The power factor as shown in Fig. 14 steadily increased up to about 100 degrees, where its value was slightly less than 1 per cent. At this stage the temperature effect in raising the power factor was somewhat greater than the lowering of the power factor due to the driving off of moisture by increasing temperature. Above 100° C. the temperature effect became more predominant until 118° C. was reached, where the power factor reached 2.6 per cent., after which moisture was rapidly released and the power factor fell to 1.3 per cent. at 120° C. With further increase of temperature the power factor increased very markedly to 9.3 per cent. at 125° C., the highest temperature to which the oil was heated. By maintaining the oil at this temperature, the power factor was brought down to 1.4 per cent., where it practically remained constant for a period of at least one hour, during which observations were continued. The curve for descending temperature was smooth and lies below the lowest points for ascending temperatures.

A plausible explanation of these maxima would be that at the first maximum, water which exists as a mixture in the oil in minute droplets was given off. At the next maximum, moisture in true solution in the oil was released. Chemical considerations would necessitate a higher temperature for the removal of the dissolved oil than for the mixed oil. Since the curves of Fig. 13 show that practically the original amount of moisture was reabsorbed upon standing at room temperature, the relative values of these maxima may indicate the relative values of mixed and absorbed moisture.

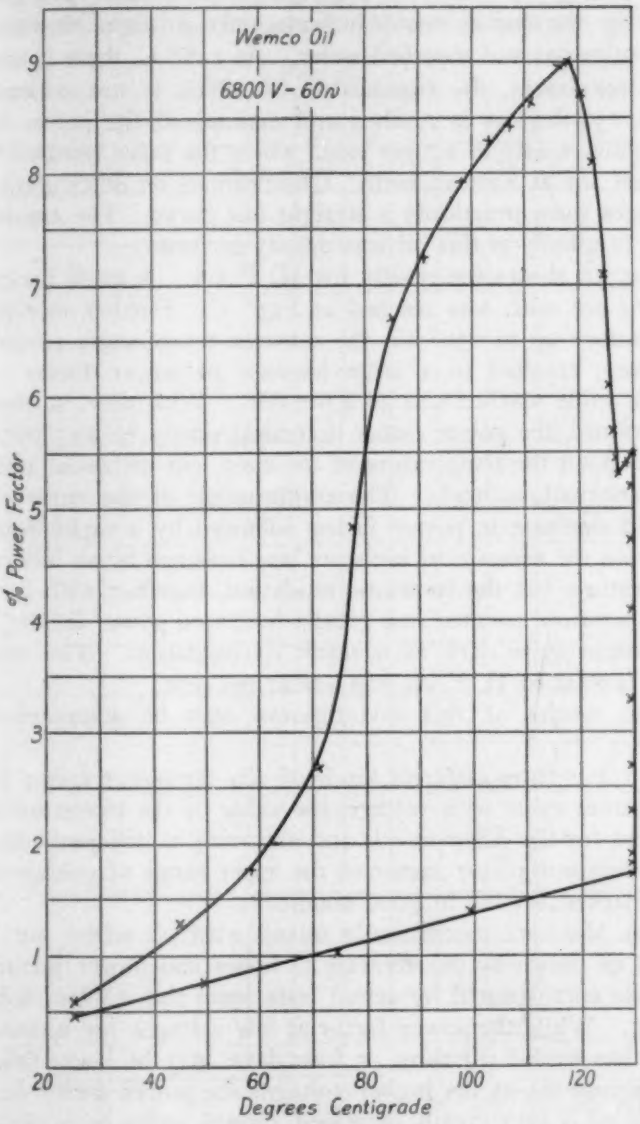
Tests in the same manner were made on Wemco A and H. F. transformer oil, both of which have a higher viscosity. Preliminary tests showed that a temperature of 125 degrees was not sufficiently high to drive off the greater part of the moisture

FIG. 14.



in these oils, which fact may be associated with the higher viscosity. When 125° C. was reached the power factor was still quite large, and changed but slowly with time. Hence a new set of

FIG. 15.



observations was taken, adjusting the oven so that the temperature would become constant at 130° C.

Fig. 15 shows the results for Wemco A oil. A maximum

is reached at 119° C. with 9 per cent. power factor. The gradual hump in the curve would indicate only a slight demarcation between mixed and absorbed water. At 128° C. there is another slight maximum, the significance of which is not understood. When 130 degrees is reached and maintained the power factor falls quite rapidly to 1.7 per cent., where the value remains fairly constant for at least an hour. Observations on descending temperatures show practically a straight line curve. The amount of water originally in this oil was 0.0023 per cent.

Fig. 16 shows the results for H. F. oil. A small maximum of 3.74 per cent. was reached at 123° C. Further increase of temperature up to 130° C., the constant temperature reached by the oven, resulted in a large increase in power factor. The highest value reached was 36.4 per cent. With time, at constant temperature, the power factor decreased slowly to 29.5 per cent. At this point the temperature of the oven was increased and further observations made. The continuation of the curve shows a slight decrease in power factor followed by a rapid decrease. No doubt the removal of moisture was hastened by an increase in temperature, but the increased oxidation, together with increase in temperature, resulted in a greatly increased power factor. The oil became quite dark as a result of oxidation. The original water content of H. F. oil was 0.0041 per cent.

The results of this investigation may be summarized as follows:

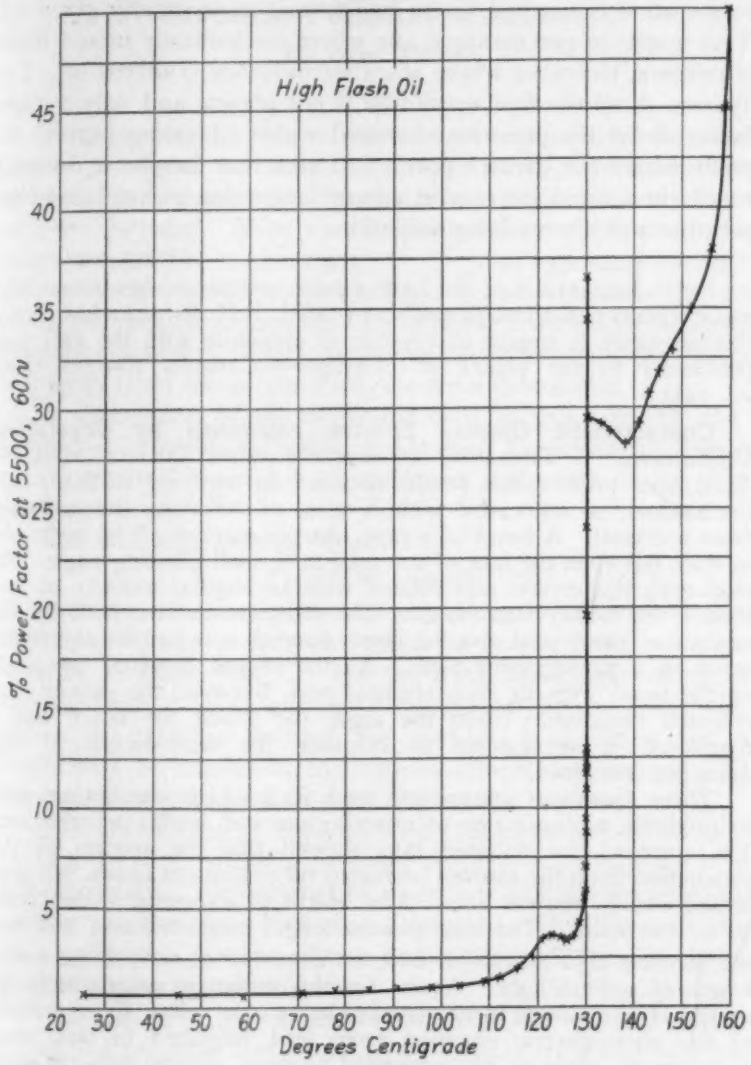
(1) For three different kinds of oils the power factor shows a minimum value with voltage, the value of the minimum being different for the different oils and occurring at different voltages. The increase in power factor on the upper range of voltage is not very marked for oil in good condition.

(2) Moisture mechanically mixed with oil settles out from the oil as shown by the decrease in losses and power factor and this was corroborated by actual tests upon the oil for moisture content. While the power factor at low voltages for washed oil, which has settled for three or four days, may be lower than for the original oil, at the higher voltages the power factor for the washed oil is very greatly increased, though water determinations show approximately the same water content.

(3) Moisture is driven from oil by heating. This is shown by a slight decrease in power factor with temperature up to a

certain temperature, depending upon the kind of oil, as well as by actual moisture determinations. As the temperature of an oil

FIG. 16.



is reduced, moisture is again reabsorbed from the atmosphere so that as room temperature is again reached almost the original

amount is taken up. When oil is being heated and power factor determinations are made during the heating so that equilibrium conditions are not established, the power factor increases until a temperature is reached where moisture is most rapidly given off. This results in two maxima, one where mechanically mixed water is released, the other where absorbed moisture is driven off. For Wemco A oil the first maximum is not present and only a slight hump shows the presence of mixed water. Heating beyond the point where the greater portion of moisture has been released, results in a rapid increase in power factor due to increased temperature and the resulting oxidation.

BY EXAMINATION of the Laue figures produced when monochromatic X-rays pass through mother-of-pearl, J. H. SHAXBY has shown this substance to consist of crystals of aragonite with the axis perpendicular to the planes of cleavage.—(*Comptes Rendus*, Dec. 26, 1924.) G. F. S.

Characteristic Gamma Spectra Examined by Crystalline Diffraction. J. THIBAUD. (*Comptes Rendus*, Jan. 12, 1925.)—This paper presents the results obtained by applying to the γ-rays the method, so successful with X-rays, of reflecting the radiation from a crystal. A beam of γ-rays, sharply marked off by apertures in lead, fell upon the face of a crystal at a small glancing angle. By clockwork the crystal was rotated with an angular velocity of less than 1° in twenty-four hours. The radiation thrown back by the surface of the crystal and the layers beneath was caught and registered on a photographic plate. As the crystal revolved the angle of the beam with its face changed and, likewise, the quantity of reflected radiation. From the angle for which the latter was a maximum, it is possible to calculate the wave-length of the radiation concerned.

Three sources of γ-rays were used, RaB + C, in equilibrium with its products, a preparation of mesothorium and, lastly, radiothorium. The trace of the reflected rays showed that the spectra of the γ-radiation from the sources contained no continuous bands, but presented clearly marked lines. The length of exposure varied from 40 to 200 hours. The longest wave-length measured was .168 and the shortest .052 Ångström unit, or about 1/100,000 of the wave-length of sodium light. Again, for this minimum wave-length the energy of its quantum is calculated to be 236,000 volts. From a study of the photo-electric emission from lead subjected to this same radiation the quantum was computed to equal 233,400 volts, in good agreement with the previous value. Two other rays, detected by the photo-electric effect, could not be confirmed by any trace on the photographic plate. G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THERMAL EXPANSION OF ALUMINUM AND VARIOUS IMPORTANT ALUMINUM ALLOYS.[1]

By Peter Hidnert.

[ABSTRACT.]

THIS paper gives data on the thermal expansion of four samples of aluminum and fifty-one samples of important aluminum alloys. The preparation, chemical composition, heat treatment, etc., are included. Most of the specimens were examined from room temperature to about 500° C. Typical expansion curves of the various groups of samples are shown and discussed. In some cases, the data on expansion were compared with the equilibrium diagrams of binary alloys. After the expansion tests, the changes in length from the original lengths were determined.

A description of the apparatus used in this research and a review of available information obtained by previous observers on the thermal expansion of aluminum and some of its alloys, are given.

The following average equation

$$L_t = L_0[1 + (22.58t + 0.00989\,t^2)\,10^{-6}]$$

is given as the most probable second-degree equation for the expansion of cast aluminum (99.95 per cent.) from room temperature to about 610° C. For the aluminum-copper alloys containing from 4 to 12 per cent. copper, a figure is given which shows the relations between the chemical composition and the coefficients of expansion for various temperature ranges. The curves indicate maxima at 6 or 8 per cent. copper.

The coefficients of expansion of aluminum-silicon alloys (4 to 12.5 per cent. silicon) generally decrease with increase in the silicon content. Two normal 12.5 per cent. silicon alloys exhibited certain peculiarities which were discussed. Duplicates of these alloys, modified by the addition of 0.1 per cent. metallic sodium, did not show these phenomena.

The expansion curves of two aluminum-zinc alloys containing 77 and 95 per cent. zinc, respectively, indicated anomalous expan-

* Communicated by the Director.

[1] Scientific Papers, No. 497. Price, fifteen cents.

sions at constant temperature (about 270° C. on heating), due to a transformation by the formation of β constituent. From the results of previous observers and the present research, it is evident that the alloy of eutectoid composition (about 79 per cent. zinc) shows the greatest change in expansion at the transformation or eutectoid temperature, and that in alloys containing from about 35 to 99 per cent. zinc, this anomalous change decreases with decrease in the amount of eutectoid contained.

The addition of 1 or 2 per cent. manganese (or 1 per cent. manganese and 2 per cent. copper) to commercial aluminum caused a decrease in the coefficients of expansion. The coefficients of expansion of the samples of aluminum-manganese alloys containing about 2 per cent. manganese are generally less than those containing 1 per cent. manganese.

A triangular diagram is shown which indicates the effect of change of composition on the coefficients of expansion of aluminum-silicon-copper alloys lying near the aluminum corner of the ternary system. For the aluminum-silicon-copper and aluminum-silicon-copper-manganese alloys investigated (containing from 84 to 94 per cent. aluminum), the coefficients of expansion decrease with increase in the silicon content. In general, the substitution of approximately 1 per cent. manganese for a corresponding amount of aluminum in aluminum-silicon-copper alloys containing from 87 to 94 per cent. aluminum, caused a decrease in the coefficients of expansion. A decrease in the coefficients also generally occurred on the substitution of 1 per cent. manganese and 2 per cent. copper for an equal amount (3 per cent.) of aluminum in aluminum-silicon alloys containing from 91 to 97 per cent. aluminum.

The coefficients of expansion of a number of samples of duralumin in various conditions were derived. In hard-rolled alloys and duplicates that were heat treated, the coefficients on second tests are less than those obtained on the first tests. For the heat-treated alloys the difference between the coefficients of the first and second tests is generally less than in the hard-rolled alloys.

The thermal expansion of cast "veritile" (Al 95.5, Ni 1.5, Cu 1.0, Cr 1.5, Mn 0.5), between 14 and 302° C., is represented by the following empirical equation:

$$L_t = L_0[1 + (21.05t + 0.01473\,t^2)\ 10^{-6}]$$

In conclusion, a comparison of the average coefficients of

expansion of the materials investigated is given for several temperature ranges in Table I. For values of individual samples over various temperature ranges (between 20 and 500° C.), reference should be made to the proper sections of the paper.

TABLE I.

Average Coefficients of Expansion of Aluminum and Various Aluminum Alloys.

Series.	Aluminum Content.	Average Coefficients of Expansion per °C.		
		20 to 100° C.	20 to 200° C.	20 to 300° C.
	Per cent.	× 10^{-6}	× 10^{-6}	× 10^{-6}
1. Aluminum { (*a*) Pure aluminum	99.95	23.8	24.7	25.7
1. Aluminum { (*b*) Commercial aluminum	99.15	23.9	25.9	26.7
2. Aluminum-copper alloys	87 to 95	22.2 to 24.6	23.6 to 26.8	26.4 to 29.2
3. Aluminum-silicon alloys	87 to 95	19.2 to 22.2	20.2 to 23.2	22.2 to 24.8
4. Aluminum-zinc alloys	5 to 86	24.3 to 33.3	27.3 to 37.2	28.3 to *40.7
5. Aluminum-manganese and aluminum-manganese-copper alloys	96 to 98	23.1 to 23.8	24.2 to 25.7	25.5 to 26.9
6. Aluminum-silicon-copper and aluminum-silicon-copper-manganese alloys	84 to 94	20.4 to 23.4	21.3 to 23.9	22.1 to 24.4
7. Duralumin	94 to 95	21.9 to 23.8	22.9 to 26.0	24.7 to 26.9
8. Veritile	95.5	23.2	24.2	25.0

* From 20 to 250° C.

EFFECT OF STRESS ON THE MAGNETIC PROPERTIES OF STEEL WIRE.[2]

By R. L. Sanford.

[ABSTRACT.]

THE work described in this paper is a part of a more extended investigation on non-destructive methods of testing wire rope. Previous methods have yielded results which were very difficult of interpretation. It is believed that this difficulty is due largely to the effects of stress which has a marked influence on the magnetic properties of steel.

Since Kennelly's law of reluctivity expresses the magnetic properties of steel by means of a simple mathematical expression and since it was desired to obtain quantitative results if possible, the problem has been studied in terms of the reluctivity relationship.

It was found (1) that upon application of a tensile stress

[2] Scientific Papers, No. 496. Price, five cents.

the reluctivity line was no longer straight as is the case for pure homogeneous materials, and (2) that the departure from straightness increased in degree as the tensile increased.

A method of analysis was worked out by means of which the observed curve could be represented by two components in each of which the reluctivity is a linear function of the magnetizing force. It is believed that this method of analysis can be further developed and its use extended to other fields of magnetic analysis.

AN ANALYSIS OF THE DEFORMATION OF THE MOORING SPINDLE OF THE SHENANDOAH.[1]

By L. B. Tuckerman and C. S. Aitchison.

[ABSTRACT.]

THE results of the examination and tests on the bent mooring spindle of the U. S. Navy Airship *Shenandoah* to determine the wind forces to which the ship was subjected during a storm on the night of January 16, 1924, are presented.

The tests were made at the request of the Bureau of Aeronautics, Navy Department.

Although the forces which produced a permanent deformation in the structure can not, in general, be determined with accuracy, an approximate method of examination and analysis is developed, applicable in the case of a ductile material to any axially symmetrical deformed structure.

The data needed for such an estimate are the extent of the observed deformation and either the residual stresses or the forces necessary to restore the form of the structure. The latter method was used in this analysis.

To obtain the permanent deformation the spindle was mounted in a lathe and by means of micrometers maximum and minimum distances that the spindle was off centre were determined for various stations along its length.

The curvature of the axis was determined by what was in effect a double differentiation of observed data. First and second differences were computed from the observed off-centre readings. These, in turn, were smoothed and a smoothed off-centre curve obtained, which gave a fair representation of the observed off-centres.

[1] Technologic Papers, No. 270. Price, ten cents.

The second differences represented, then, the approximate curvature of the spindle at each station and though subject to large errors, it is believed that they do not appreciably affect the location of the maximum curvature, which would also be the location of maximum stress.

The law of plastic flow above the yield point of the material was assumed to take place at a rate roughly proportional to the excess of stress above that point. It was also assumed that the load, under which the spindle was bent, was applied suddenly, as with a sudden jerk, and also that the reactions occurred at the bearings through which the spindle was attached to the ship.

Based on the above assumptions and by the use of simple theory a moment distribution was found which gave a fair representation of the load distribution which bent the spindle.

The spindle was then placed in a testing machine and the calculated moment distribution duplicated. The load was first applied in the same direction as the original wind load to secure an estimate of the range of elastic deformation as free as possible from the previous deformation. At a load of 17,000 pounds, corresponding to a reaction of 9880 pounds at the mooring attachment, a further permanent deflection of 0.003 inch was observed. A wind load of 10,000 pounds would, therefore, have produced a small permanent deflection in the spindle. The corresponding extreme fibre stress is 28,300 lb./in.^{2}. The material evidently met the specification requirements of 28–36,000 lb./in.^{2} yield point.

The spindle was then turned over and approximately straightened under steady load. Permanent deflection became noticeable at a load of 8000 pounds (showing the effect of previous overstressing in the opposite direction) and increasing rapidly with the load. The loading was carried to 23,100 pounds, corresponding to a reaction of 13,400 pounds at the mooring attachment and an extreme fibre stress of 38,400 lb./in.^{2}.

The spindle was again mounted in the lathe and off-centre distances obtained as before. The amount that the spindle had been straightened was obtained.

Analysis showed that the difference between the original bending and the straightening was of the kind to be expected from the difference between a suddenly applied and a slowly applied load.

It was found that the material of the spindle evidently met specification requirements for yield point; that the axis of the

spindle bent elastically approximately 0.14 inch out of line for each 10,000 pounds of load applied at the mooring attachment; and that the load was certainly greater than 13,400 pounds, the steady load that produced the straightening in the testing machine; and probably greater than the 27,000-pound estimate by the rough theory.

MEASUREMENT OF ELECTRICAL RESISTANCE AND MECHANICAL STRENGTH OF STORAGE-BATTERY SEPARATORS.[1]

By L. C. Snyder.

[ABSTRACT.]

THE life and internal resistance of a storage battery depend largely upon certain properties of the separators, usually of wood, that are placed between the plates of the battery. The electrical resistance of the separators and their mechanical strength are important factors.

The electrical resistance of the separators was measured by placing a specimen in an electric circuit consisting of two branches supplied by a transformer having two secondary windings. The current from one of the secondary windings was passed through a known area of the separator to be measured. The current from the other winding was passed through a slide wire and resistance box which served as a potentiometer. The accuracy of the method was well within 1 per cent., and since the resistance of the different samples of the same kind varied by as much as 15 per cent. the accuracy of the method was sufficient for the purpose.

The measurements of mechanical strength were made on narrow strips cut from the separators. The test specimens were broken in a tensile strength testing machine after having been subjected to treatment similar to use in a battery.

The results of the measurements of the resistance and the mechanical strength show the effects produced by the different conditions to which the samples were subjected. The results, in general, are as follows:

Electrical Resistance.—(*a*) The resistance was found to change for some time after immersion, but became practically constant after two or three weeks.

[1] Technologic Papers, No. 271. Price, ten cents.

(*b*) The resistance was proportional to the resistivity of the acid in which the sample was immersed.

(*c*) The resistance of the separators treated by the caustic-soda method was lower than for like samples treated by the steam method.

(*d*) The temperature coefficient of resistance was approximately the same as the coefficient of resistivity for sulphuric-acid solutions of the same density.

(*e*) The resistance of samples of different thicknesses, but identical in other respects, was approximately proportional to their thickness.

(*f*) The resistance of the sawn separators was smaller in most cases than that of the rotary cut samples.

Mechanical Strength.—(*a*) Immersion in acid solutions was found to weaken the wood fibres. The strength decreased with time of immersion and concentration of the solution. Above the specific gravity of 1.300 the action was severe.

(*b*) The strength decreased with increase of temperature of the acid solution.

(*c*) The strength was approximately proportional to the thickness of the samples.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR MILLED TOILET SOAP.[5]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the soap committee of the soap section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on November 5, 1924. The specification covers one grade of soap made of high-grade materials, and gives the general requirements and detailed methods of inspection and testing, the preparation of the reagents required, and the basis of purchase. The methods of inspection and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under the specification is a high-grade, milled

[5] Circular No. 194. Price, five cents.

cake soap, as free as possible from water, either colored or uncolored, and unscented or perfumed in a manner indicated in the contract, thoroughly saponified, well compressed in firm, smooth cakes of a size and shape specified in the contract. It should lather freely when used with cold water. Bidder shall state weight and number of cakes in each box.

The detail requirements are:

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 15 per cent. Deliveries which yield more than 15 per cent. of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 1.5 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1 per cent.

Matter insoluble in water shall not exceed 0.2 per cent.

Unsaponified saponifiable matter shall not exceed 0.3 per cent.

Rosin, sugar, and foreign matter shall not be present.

The color, odor, and character of the soap must be as specified by the purchaser. The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 15 per cent. of matter volatile at 105° C.

UNITED STATES GOVERNMENT MASTER SPECIFICATIONS FOR POWDERED SOAP (FOR LAUNDRY USE).[6]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the soap committee of the soap section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on November 5, 1924. The specification covers one grade of soap made of high-grade materials, and gives the general requirements and detailed methods of inspection and testing, the preparation of the reagents required, and the basis of purchase. The methods of inspection and testing were prepared by a committee of the American Chemical Society in coöperation

[6] Circular No. 195. Price, five cents.

with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a soap in powdered form made from soda and fats, without rosin, as free as possible from water and all substances other than true soap, of a light uniform color, free from disagreeable odor, and suitable for high-grade laundry work with soft water, when the presence of alkaline salts is objectionable. Bidder shall state size and weight of package.

The detail requirements are:

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 7 per cent. Deliveries which yield more than 7 per cent. of matter volatile at 105° C. will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol, and sodium chloride shall not exceed 3 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 0.4 per cent.

Titer of the mixed fatty acids prepared from the soap shall not be less than 39° C.

Residue retained on a No. 12 sieve shall not exceed 1.5 per cent.

Color and odor shall be as specified. The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 5 per cent. of volatile matter.

On the Permanent Electret. Mototaro Eguchi. (*Phil. Mag.*, Jan., 1925.)—"'Electret' is the name given to the dielectric which is electrized permanently by a special treatment due to the author. Some waxes and resinous materials have moderate conductivity in their liquid state, while they are very good insulators in the solid state. The electrical conductivity of these materials varies gradually with the degree of solidification, and when the materials get moderately hard the conductivity becomes practically nil. The author let solidify a mixture of these materials in a strong electric field applied through all the time in which the solidification went on. The dielectric taken out of the field, after having been cooled sufficiently, showed very strong polarities on its two surfaces which were kept in contact with the electrode plates during the preparation. The elec-

trization of such a dielectric could not be destroyed by several treatments, such as touching by Bunsen flame, exposure to X-rays, planing with knife, washing with some solvents, etc. Nor did it die away after the lapse of many years. From several subsequent studies, it has become evident that the electric change of the dielectric is not of a superficial nature, but that it is a permanent internal change within the material." For dielectric he used a mixture of equal parts of carnauba-wax and resin. To this some beeswax might be added. If a thin disc of this material had its upper surface connected to the positive pole of a high-tension machine and the lower surface to the negative, there appears a negative charge on the upper surface and a positive charge on the lower one soon after the completion of the charging process, but in a day or two these charges are reversed in sign. These new charges grow to full strength in a few days, and after years have not decayed. All the methods of discharging mentioned above resulted in a loss at first of the charge on the surface, but it always came back later.

The surface density of the charge on the surfaces of one electret made in 1919 was about 6 E.S.U. per sq. cm. This is somewhat larger than the highest surface density to be reached by the rubbing of sulphur, shellac and sealing-wax.

"From many experimental studies made by the author, the internal electrical change of the permanent electret was concluded to be of the nature of 'polarization,' *i.e.*, every portion from element to element of the dielectric material was in the state of having acquired equal and opposite electrical polarities on its two ends." Thus from Japan there comes an electrical analog to the permanent magnet.

G. F. S.

Para-nitrobenzoic Acid as an Acidimetric Standard.—Benzoic acid having been shown by experience to be an excellent primary standard for acidimetry, THORNTON and GETZ, working in the Johns Hopkins Chemical Laboratory, have experimented with the 1–4 nitro-derivative of the acid with a view to determine its suitability for such purpose. The methods used and the results are given in a paper in the *Amer. Jour. Sci.* ([5], 1925, **9**, 176). The investigation was comprehensive and thorough. The conclusions are as follows:

Para-nitrobenzoic acid proves to be an accurate primary standard in neutralization processes. It is readily purified—two or three crystallizations from alcohol being all that is necessary when one starts with material of fair quality. Not being bulky, it is easy to weigh and transfer. It requires no fusion, mere drying at 120°, which is far below its melting point, being sufficient. It does not seem to be more than ordinarily hygroscopic—a possible point of superiority as compared with benzoic acid. Its high molecular weight permits taking large samples with the attendant increase in accuracy.

H. L.

NOTES FROM NELA RESEARCH LABORATORIES.*

THE TRUE TEMPERATURE SCALE AT INCANDESCENCE AND THE MELTING POINT OF MOLYBDENUM.

By A. G. Worthing.

[ABSTRACT.]

Spectral emissivities of Mo from 300° K. to its melting point have been obtained for 0.665μ and 0.475μ by three methods, *viz.*, (1) by observing the ratio of the outer surface brightness of a Mo tube heated to incandescence to the interior brightness as seen through small holes in its side walls; (2) by observing the ratio of the spectral brightness of Mo to W on opposite sides of a fused junction formed by welding a Mo and a W filament end to end, and then multiplying the ratio by the previously determined spectral emissivity of tungsten, and (3) by measuring the spectral reflectivity of Mo ribbon filaments and taking the differences between the observed value and unity. The results obtained by all three methods agree very well. For 0.665μ the spectral emissivities at 300° K., 1500° K. and 2800° K. are 0.419, 0.371 and 0.331; for 0.475μ, 0.424, 0.390 and 0.365. These values are without exception lower than corresponding previously published values. Causes for this discrepancy are discussed and reasons advanced for the reliability of the data here given.

Spectral Reflectivities of Mo at Room Temperature.—For very pure specimens at .665μ and 0.475μ, the values 0.580 ± .006 and 0.576 ± .007 have been obtained. No dependence on previous heat treatment was found.

Temperature Scale of Mo.—These spectral emissivities lead to a difference between true temperature and brightness temperature as a function of the brightness temperature of 46° at 1000° K., 113° at 1500° K., 217° at 2000° K. and 370° at 2500° K.

The melting point of Mo has been obtained by three methods, *viz.*, (1) by observing the brightness temperature of a Mo filament at melt and applying the observed spectral emissivity, (2) by observing the brightness temperature of partially molten Mo arc terminals at the boundary between the solid and liquid phases

* Communicated by the Director.

and then applying the observed spectral emissivity, and (3) by observing the temperature of a tungsten filament just next to its unfused junction end to end with a Mo filament, as the junction is heated up to the melting point of the Mo. The rounded average of a large number of determinations yielded 2895° K. ± 10 ($c_2 = 14{,}330\mu$ deg., $T_{Mo} = 1336°$ K.). This value is generally higher than the results of others.

A CAPILLARY MANOMETER SYSTEM FOR PREPARING MIXTURES OF GASES WITH A VERY HIGH RATIO BETWEEN COMPONENTS.

By Elliot Q. Adams and E. R. H. Charpentier.

[ABSTRACT.]

CAPILLARY manometers are used to measure gas flows by introducing in the line as a resistance to the flow a piece of capillary tubing, and so creating a difference in pressure which is read on a U-tube manometer, the ends of which are sealed to the ends of the capillary.

A capillary manometer has been constructed in which the capillary is in a vertical position; a great saving in desk space is thus attained over the usual type in which the capillary is horizontal.

The capillary tubing is sealed to one branch of a U-tube containing the manometer liquid, the other branch being bent over and sealed to the upper end. A stopcock is sealed to the top of the bend, through which the gas escapes; the gas enters from behind through a tube sealed to the U-tube just below the capillary. A tubulated test-tube serves as manometer liquid reservoir, and is attached through a rubber stopper to a stopcock sealed to the lower bend of the U-tube. The manometer is filled by blowing into the tubulated test-tube. The apparatus is fastened to a board which for permanent installations may be fastened to a table. A scale for reading difference in manometer liquid levels is fastened to the board. The apparatus is graduated by measuring, for several different levels of the liquid in the U-tube, the corresponding amount of gas which flows through the capillary in a given length of time.

Several manometers giving different rates of flow (*i.e.*, different sized capillary resistances) can be mounted on the same board.

It has been found, however, that mounting manometers in pairs on one board is very convenient.

Manometers of the described type were constructed in connection with work on the effect of oxygen concentration on the chemiluminescence of phosphorus where a ratio of components of 1 to 1,000,000 was required. The system used comprised three pairs of manometers. One manometer in each pair received pure nitrogen, excess gas escaping through a "spill bottle." The smaller manometer of the first pair received oxygen, the excess escaping through a "spill bottle"; the smaller manometer of the two remaining pairs was supplied with the mixture from the preceding pair, the excess gas being spilled as before.

Dielectric Constants of Conductors. REINHOLD FUERTH. (*Phys. Zeit.*, Dec. 15, 1924.)—The measurement of this physical property in conductors is beset with many difficulties. By definition the dielectric constant of a substance is the ratio of the capacity of a condenser having the space between its plates filled with the substance to the capacity of the same condenser filled with air. The very definition therefore indicates a method of measuring the constant, *viz.*, a condenser is filled with the substance under investigation and its capacity is then determined. The method works well for insulators, but a condenser filled with a conductor discharges promptly. This compels the use of alternating currents of such high frequency that during a period the condenser has little chance to discharge. The greater the conductivity of the substance the higher must be the frequency of the current. It is known that the dielectric constant is a function of the frequency of oscillations employed instead of being a real constant. Hence results obtained by this method are of limited range. A second method consists in measuring the force exerted in an electric field upon a limited portion of a substance. It is with mathematical difficulties that this plan is confronted in the case of conductors, but the author has found a special instance in which the problem can be adequately solved. Between two vertical and parallel metal plates a conducting liquid to be investigated is placed. In it a torsion thread supports an ellipsoid of rotation, with the axis of rotation horizontal and making an angle of 45° with the plane of the plates. Upon the application of an electrical field to the plates the axis strives to set itself parallel to the plates and the force in play is measured by the torsion of the thread. When the moment of torsion is known, the dielectric constant of the liquid can be calculated from the dimensions of the ellipsoid and from the ratio of the conductivities of the ellipsoid and of the liquid. The dielectric constant of the ellipsoid is not needed. "This fact and the further circumstance that the two conductivities come

quantitatively in evidence in the final formula depend upon the suspended body being an ellipsoid."

In the actual experiment a nickel ellipsoid with the ratio of its axes 1 : 20 was suspended by a quartz thread. An alternating potential of 50 cycles per second was applied to the plates. For water the values of the dielectric constant measured by this method ranged from 76 to 82 and seemed to be the same for distilled and for spigot water. Solutions of cane sugar in water were measured and showed a decrease in the constant with increasing sugar content. A series of experiments on solutions of NaCl in water was carried out. The highest concentration reached was .1 per cent. More concentrated solutions presented difficulties owing to the development of gases and convection currents. Two alternating potentials were used of 15 and of 30 volts, respectively. With both potentials the dielectric constant grew less at first as small quantities of NaCl were added to water, dropping for the smaller voltage to about 55. Further addition of salt caused the constant to increase. Except for very small concentrations the constant for 15 volts is roughly 17 less in value than for 30 volts. This variation with the voltage used may well explain the discrepancies between previous published results. G. F. S.

The Velocity of Sound and the Ratio of the Two Specific Heats of Certain Organic Liquids. W. BUSSE. (*Ann. d. Physik*, No. 22, 1924.)—Kundt developed the method of examining the vibration of air in a tube by having the longitudinal waves record their motion in arranging powders placed in the tube. Doersing later extended the method to liquids and the present paper gives an account of improvements in his technic. As an indication of the accuracy attained, let it suffice that, of ten determinations of half the wave-length concerned, six values were equal to 13.1 cm., two to 13.2 cm., and one each to 13.175 and 13.133 cm. Of the fifteen organic liquids examined aniline had the highest sound velocity, 1675.7 m. per sec. The ratio of the specific heats is calculated by two formulas which are found to give results in good agreement.

G. F. S.

"Electrolytes" and "Ionogens." W. BLUM. (*Amer. Electrochem. Soc.*, Niagara Falls Meeting, 1925.)—Considerable confusion exists in the use of the term "electrolyte." Salts, such as NaCl, KCl, etc., are called "electrolytes," and electrically conducting solutions of these salts are likewise called electrolytes. It is therefore proposed to confine the use of the term "electrolyte" to the conducting solutions or conducting media, and to adopt the term "ionogen," suggested by Alexander Smith, to mean any salt or chemical compound capable of forming ions.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

GRAIN SIZE AND DISTRIBUTION IN EMULSIONS.[1]

By S. E. Sheppard.

[ABSTRACT.]

REPLY to F. F. Renwick (*Phot. J.*, **64**, 324, 1924). Three facts are presented as fundamental to a consideration of the subject: (1) Primary grains in silver bromide emulsions form a statistically definite order of single crystals. (2) Size distribution can be represented by probability functions. (3) Crystals are individuals and not aggregates. Clumps demand separate consideration.

Assuming the Maxwell distribution function to be primarily applicable and the rate of growth of a particle to be proportional to its total surface, or approximately its projective area, the formula

$$y = Ae^{-k\ln(x-a)^2}$$

accurately represents all emulsion-grain distributions measured. In the mechanism of precipitation in polar substances such as silver halide, there may be elastic or inelastic collision depending upon the relative charges on the colliding surfaces. Renwick's explanation of silver bromide grain formation as an electrical phenomenon is not satisfactory. Electrostatic aggregation, including single ions, is one step in the process of grain growth. Rearrangement of adherent particles as demanded by the principle of minimum surface energy has some bearing on the matter. The re-orientation of adsorbed complexes probably has a large effect, certainly in sections small enough to be unaffected by convection. This problem may be studied in two systems, one where there is no convection or stirring and the other where there is total control of convection. Rhythmic precipitation in gels exemplifies the first condition, as also does the periodic formation of silver iodide on the surface of an iodized collodion plate when

* Communicated by the Director.

[1] Communication No. 213 from the Research Laboratories of the Eastman Kodak Company and published in the *Phot. J.*, **65**, 31, 1925.

being bathed in silver nitrate. A section through each zone of a series of Liesegang rings should show a grain-size distribution forming a reproducible unit of a periodic series. The effect of stirring is to destroy this periodicity.

RUBBER LATEX PARTICLES.[1]

By E. P. Wightman and A. P. H. Trivelli.

A BRIEF note describing the motion picture method of examining rubber latex particles, and discussing the work of Hauser in relation to the shape of the latex particles.

The pear shape, similar to the Hevea latex particles, described by Hauser, appears to be quite frequent, but the particles do not remain in this shape. They may change more or less quickly to another shape, split off a new particle, or add on a smaller particle.

To explain the formation of an ellipsoidal particle and the splitting off of a section of particle is quite simple if a tangential impact causing the particle to spin is imagined. If this rotational motion is strong enough, the particle will elongate until the surface tension is not sufficiently strong to draw it back into spherical shape or even to hold it together. Thus, new particles will be formed. A particle moving rapidly for any reason will tend to take the pear shape. Here again it is easy to split off a section of the particle. Two particles will join each other if they come together with sufficient momentum. The larger the particle, the easier it is to deform or break it.

The Spark Spectrum of Tungsten in the Schumann Region. L. and E. BLOCH. (*Comptes Rendus,* Jan. 12, 1925.)—Here are tabulated 360 lines, ranging in wave-length from 1826 to 1453 Ångström units and a promise is given of the publication of additional lines to bridge the gap up to 1873, to which length the measurements of Bayen extended. Since Bohr's theory has furnished an explanation of the wave-lengths of the lines of hydrogen, it will at some time be a duty to search for a quantitative elucidation of the origin of each of these many lines. In view of the complexity of the tungsten atom with its scores of planetary electrons moving about the central nucleus, this will be no light task and may well baffle for a shorter or a longer time a hardy investigator, even though he be armed with a most modern mathematics. G. F. S.

[1] Communication No. 215 from the Research Laboratories of the Eastman Kodak Company, and published in the *Ind. Eng. Chem.*, 17, 164, 1924.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

VITAMIN A CONTENT OF FRESH EGGS.[1]

By Joseph C. Murphy and D. Breese Jones.

[ABSTRACT.]

A SERIES of experiments was undertaken to ascertain the smallest quantity of fresh, whole egg which will cure rats of xerophthalmia, and enable them to grow at a normal rate. It was found that from 0.50 gram to 0.75 gram of fresh, whole egg fed daily supplies young rats with sufficient vitamin A for growth at a normal rate. A smaller quantity, 0.25 gram, was adequate to cure well-advanced cases of xerophthalmia.

THE EFFECT OF LONG-CONTINUED STORAGE AT LOW TEMPERATURE ON THE VITAMIN-A CONTENT OF EGGS.[2]

By D. Breese Jones, Joseph C. Murphy and Otto Moeller.

[ABSTRACT.]

AN investigation was undertaken by the Bureau of Chemistry to ascertain the effect of long-continued storage at low temperature on the vitamin-A content of hens' eggs. The results of the feeding experiments showed that no serious deterioration took place in the vitamin-A content of the eggs held in storage for nine years in a frozen condition. In 0.25-gram daily doses, the storage eggs were as effective as fresh eggs in curing xerophthalmia. Even 0.1 gram daily caused noticeable improvement in the condition of the eyes, arrested the decline in weight, and caused a moderate resumption of growth, which continued for two to five weeks. The somewhat poorer results obtained with the storage eggs than with the fresh eggs suggest that a slight deterioration may have taken place during the period of storage. However, when the difficulties and possible sources of error involved in the present available methods for estimating

* Communicated by the Chief of the Bureau.

[1] Published in *J. Agr. Res.*, **29** (Sept. 1, 1924): 253.

[2] Published in *Am. J. Physiol.*, **71** (Jan., 1925): 265.

vitamin A are considered, such slight differences as were found in the vitamin-A content of the fresh and storage eggs cannot be very significant.

INFLUENCE OF MERCURY AND OTHER IMPURITIES ON THE RATE OF OXIDATION OF WHITE ARSENIC BY NITRIC ACID.[3]

By C. M. Smith and G. E. Miller.

[ABSTRACT.]

IN THE usual method of manufacturing calcium arsenate from lime and white arsenic, the latter is oxidized to arsenic acid by means of nitric acid. The rate at which this oxidation progresses varies widely with different lots of material, causing delay and increased cost in the manufacture when a sluggish lot is encountered. This behavior has been traced to the presence of small quantities of mercury in the white arsenic, 0.01 per cent. being a powerful negative catalyst. Reactivity may be restored in such cases by the addition of small quantities of hydrochloric, hydrobromic, or hydriodic acids. These compounds, even in the low concentrations necessary, may, however, be corrosive to the metallic vessels in which the oxidation is frequently accomplished.

PREPARATION OF BRILLIANT CONGO R ("VITAL RED") AND THE SUITABILITY OF VARIOUS SAMPLES OF VITAL RED FOR BLOOD-VOLUME WORK.[4]

By Samuel Palkin and Herbert M. Evans.

[ABSTRACT.]

AN improved process has been developed for the synthesis of Brilliant Congo R (Vital Red). This process includes (1) the preparation or purification and the quantitative estimation of the intermediates, tolidine amino R salt, and Brönner acid; and (2) the preparation and purification of the dye itself.

Some of the improved features of the revised process, which is based on the German patents, are (1) separation of a "half-dye" addition product of tetrazo-tolidine with amino R salt; (2) a more careful control of temperature, hydrogen-ion concentration, and proportions of reacting constituents; (3) the use of

[3] Published in *Ind. Eng. Chem.*, **16** (Nov., 1924): 1168.

[4] Published in *J. Am. Chem. Soc.*, **47** (Feb., 1925): 429.

an excess (1 molecular equivalent) of Brönner acid, instead of the theoretical equivalent; (4) elimination of heat and alkali treatments necessary in former processes to render the dye soluble.

As shown by practical clinical tests, the dye prepared by this process is suitable for blood-volume determinations.

The Spectrum of the Aurora Borealis and the Higher Regions of the Atmosphere. L. VEGARD. (*Phys. Zeit.*, Dec. 15, 1924.)—Every normal man loves a fight whether it be a battle of weapons or of wits. The field of physics is far from being free from such interesting contests, and from each conflict there emerges a fact confirmed or a theory established. The discussion between Pender and Cremieu a score of years ago and that more recent one between Duane and Compton upon the change of the wave-length of X-rays by scattering will serve as illustrations. There is now a question in regard to which opinion is divergent, *viz.*, the origin of the green line of the aurora. Vegard, the Norwegian physicist, from his studies of this phenomenon came to the conclusion that solid nitrogen exists in the upper parts of the atmosphere and that it emits the green line (JOUR. FRANK. INST., Dec., 1923). To test the truth of his inference he went to the cryogenic laboratory at Leyden and there solidified nitrogen by means of liquid air. This he bombarded with cathode-rays. As to the luminous effects he says, "When the velocity of the cathode-rays exceeded a certain limit, I got an intense green glow. The spectrum showed two bands in the green, to which I have given the designations N_1 and N_2, along with a series of bands in the blue and in the violet regions. The green band N_2 was quite sharp, had a wave-length of 5230 Å.U. and was found to match a line in the spectrum that can be seen during brilliant auroral displays. The band N_1 was broader and extended beyond both edges of the strong auroral line, 5577 Å.U. It could further be seen to possess a structure wherein two maxima were recognizable. Although the lines in the green, particularly those corresponding to the auroral lines, had, under the conditions of the experiment, the character of bands, nevertheless the agreement between the spectrum of the aurora and the glow of solid nitrogen was so distinctive that I held it beyond doubt that in both cases the same peculiar effect of light was concerned." He learned, in addition, that the bombarded nitrogen gave rise to typical ultra-violet bands such as are found in the auroral spectrum, and that the distribution of intensity in them is like that in the auroral light. An agreement in the red likewise manifested itself.

It seemed that a satisfactory origin for the green line had been discovered, but at the Toronto meeting of the B.A.A.A., Aug., 1924, Professor MacLennan and G. N. Shrum presented the results of their

investigation of the spectrum of bombarded solid nitrogen that were quite in opposition to those of Vegard (this JOURNAL, Sept., 1924). They searched carefully for the 5577 green line but found no trace of it, though they did get lines or bands of nearly its wave-length. Not unnaturally Vegard is unwilling to yield his conclusion until facts beyond dispute compel him to abandon it. He puts emphasis on the very small size of the particles of solid nitrogen in the higher air. In his opinion a "pseudogas" exists there, consisting of particles of solid nitrogen that need not all contain the same number of atoms and in which the atoms are held together by such forces as normally bind together the parts of solids. He maintains that an exact agreement in wave-length is not to be expected between the bands or lines emitted by such a pseudogas and those coming from the solid nitrogen of the laboratory. He tried to realize in the laboratory the state of separation of the nitrogen particles high above the earth by solidifying a mixture of argon and nitrogen, so that each nitrogen particle was separated from its fellows by inactive solid argon. It required but little nitrogen to produce a strong spectrum of that element. Under these conditions the band N_1 grew sharper with diminishing proportions of nitrogen in the solid mixture, since two weak bands gradually disappeared while the main band (which with its fainter associates formed N_1) not only persisted, but grew nearer in wave-length to the green line of the aurora. Results of a similar character were obtained when solid argon-nitrogen was bombarded by canal rays. He found the spectrum of nitrogen in this case to contain bands of approximately the wave-lengths that have been photographed by Lord Rayleigh in the light of the sky at night. Vegard accordingly attributes such illumination of the sky to the action of canal or positive rays.

After the cathode-rays have ceased to fall on the solid nitrogen, it continues to glow for some minutes or even for much longer periods. Vegard directs attention to this as an instance of the phosphorescing of an element, a remarkable phenomenon.

If the phosphorescing nitrogen is permitted to warm up gradually from the temperature of liquid hydrogen, it glows very strongly at a certain temperature and the color of the light changes from green to blue. Simultaneously the nature of the solid changes from that of ice to a weakly coherent powder. A modification of the crystallization has occurred. From studies of the specific heat of the substance it was known that this change takes place at about 35.5° abs. After the alteration of the solid the bands N_1 and N_2 are not emitted and phosphorescence is absent. "This peculiarity of solid nitrogen has very interesting relations to cosmic phenomena. In that region of the atmosphere where the green line of the aurora manifests itself, the temperature must be below 35.5° abs. We thus get a thermometer for the highest portions of the atmosphere."

G. F. S.

NOTES FROM THE DEPARTMENT OF THE INTERIOR, U. S. BUREAU OF MINES.*

DETERMINATION OF SMALL QUANTITIES OF PETROLEUM VAPOR.

By G. W. Jones and W. P. Yant.

AMETHANE indicator has been developed by the Pittsburgh experiment station of the Bureau of Mines, designed for detecting that gas in mines, which can be used for detecting other combustible gases. The apparatus is suited to detecting small quantities of petroleum vapors. A simple portable device for use by workmen not skilled in the use of chemical apparatus, to warn them of the presence of an asphyxiating atmosphere, is needed for use about refineries and other places where vapors from petroleum are likely to be encountered.

The apparatus does not detect hydrogen sulphide, and if hydrogen sulphide is present, other means must be used for determination of that gas.

The percentages and predominating hydrocarbon content of the gases and vapors liberated by petroleum and its products while stored in tanks and similar places show that the predominating hydrocarbon gases and vapors range from ethane to duodecane; the percentages present range from only a trace (0.01 per cent.) to over 80 per cent. When, however, the vapors are of higher molecular weight than heptane they are not present in quantities sufficient to produce explosive mixtures at ordinary temperatures (less than 120° F.).

The scale for petroleum vapors devised for use with the Burrell gas indicator is based on the relative explosibility of the vapor, as explosibility is the information most desired.

The 0.3 per cent. mark has been chosen as the safety limit because the presence of this proportion of vapor was intoxicating to some of the observers after exposure to it for one-half hour or more.

For testing places that are accessible, the battery used with the indicator is strapped about the waist, the indicator carried in the hand, and tests are made as the user proceeds from place to place.

* Communicated by the Director, Bureau of Mines.

For sampling inaccessible places a small attachment is provided through which the samples of gas are aspirated and introduced into the indicator.

The time required for a test is about four minutes, and twenty or more determinations can be made before a freshly charged battery becomes discharged. Actual tests with the indicator in the hands of an inexperienced user have shown it will indicate within 0.1 per cent. the amount of petroleum vapor present. Further details are shown in Technical Paper 352, just published.

HELIUM-OXYGEN MIXTURES AS A MITIGATION OF CAISSON DISEASE.

By R. R. Sayers, W. P. Yant and J. H. Hildebrand.

RECENTLY the writers have conducted experiments with animals and men breathing helium-oxygen mixtures under pressure. The object of this work was to determine whether helium-oxygen atmospheres can be utilized to advantage in place of normal air for caisson and diving work. In such work the permissible pressures and times of compression and decompression are limited by the physiological effects on man. The major effect is that the nitrogen (which is the inert constituent of normal air and is absorbed by the body tissues and fluids in abnormal amounts when under pressure) tends to form bubbles in the tissues on too rapid decompression from high pressures.

The Bureau of Mines is interested in this problem on account of the possibilities of mitigating caisson illness in tunnel construction and other engineering operations requiring men to work in compressed air. In addition the Navy Department is interested on account of the possibilities for extending the range of salvaging and marine engineering operations. The results of the experiments conducted by the writers lead to the following conclusions:

Helium is without odor or taste and has physical properties which promise to be of interest physiologically and which have been found to have possibilities of great practical use, especially in making a synthetic atmosphere that will reduce the hazard of caisson disease. The substitution of helium for the nitrogen ordinarily present in the air we breathe has been found to result in an atmosphere which is as respirable as that provided by nature. The results obtained indicate that helium not only has the advan-

tage of being less soluble than nitrogen, but also has the advantage of diffusing more rapidly in the body fluids and tissues which results in rapid elimination of the gas from the tissues during decompression. Along with mitigating the hazard of caisson illness, helium should markedly increase the scope of other kinds of engineering work in compressed air. The tests conducted by the writers indicated that through the use of helium and oxygen mixtures as a substitute for air in diving work, the time of decompression can be materially reduced. In a series of experiments on animals, after similar exposures decompression could be made from the helium-oxygen mixtures in as low as one-sixth the time necessary for air or nitrogen-oxygen mixtures. In a few preliminary experiments on men, decompression was made in one-fourth to one-eighth the time ordinarily recommended for air. These man-tests will not be described in this report as they are too few to justify conclusions regarding the final factor of advantage. The U. S. Navy Department and the Department of the Interior, Bureau of Mines, are at present carrying out coöperatively an extensive program of experiments with men.

More complete details are presented in Serial 2670 of the Bureau of Mines.

PROTECTION OF OIL-FIELD EQUIPMENT AGAINST CORROSION.

By R. Van A. Mills.

The writer has recently completed a study of the common causes and effects of oil and gas-field corrosion, and of methods for abating the damage. Data were also obtained on experiments or tests that can be conducted in the field laboratory, and will yield useful information on the character of the waters and the action to be expected.

Rapid deterioration and destruction of metal equipment in oil and gas fields cause waste of resources and financial losses that must be lessened or eliminated if operations in many important fields are to continue profitable. The magnitude of this destruction is proved by the huge consumption of iron and steel pipe, tubing, casing, pump valves, and sucker rods to replace worn-out equipment, and by the amount of such equipment that is left in wells or junked. This destruction of equipment constitutes in

itself a serious waste, but contingent production troubles, such as underground leakage of oil through defective tubing and pumps, and the consequent loss of oil and gas because of damage to pay sands by infiltrating water and silt, frequent and costly repairs with necessary suspension of production, and the ultimate injury to or loss of valuable wells, often cancel all operating profits.

Many of these troubles result from rapid destruction of metal equipment by corrosive waters. The strata penetrated by the wells usually contain saline waters. Certain types of these waters, with their associated gases, are intensely corrosive; they attack well casing or tubing so vigorously as to riddle it with holes, rendering it useless in a few years or even a few months or weeks after it is installed. Pump plungers, working barrels, balls and seats of valves and screen pipe, as well as lead lines and other surface equipment, are ruined with equal rapidity. The development and application of practical methods to retard or prevent this corrosion are among the most urgent problems of the oil and gas industry.

Although much progress has been made in preventing the corrosion of metals, the need for reducing the damage from corrosion in oil and gas fields is still imperative. This is especially true of underground corrosion in the wells, because underground conditions favor corrosion and are difficult to study; hence they have not been thoroughly understood. Further details are presented in Bulletin 233 of the Bureau of Mines.

The Influence of the Length of the Radiating Column on the Width of Spectral Lines. B. VENKATESACHAR. (*Phil. Mag.*, Jan., 1925.)—The late Lord Rayleigh pointed out the effect on the width of lines produced by the absorption taking place as the light makes its way toward the spectroscope. Here the theory is developed and then a comparison is drawn between the photographs of a certain mercury vapor green-line group made in one case from a thin layer of the vapor and in the other from a long column of it. In the latter case the lines are broadened and sometimes blend into one another. Such an effect modifies greatly the temperature estimated to belong to the source of the radiation from a study of the limit of its possible interference. In the case of hydrogen lines the temperature of the gas for a thin layer would seem to be 400° abs., while that for a layer 7.5 cm. deep would be 1120°, and for 100 cm., 2540°. The author points out that dependence of apparent temperature on length of radiating column may necessitate the reduction by some thousands of degrees of the maximum temperature assigned by Buisson, Fabry and Bourget to the nebula in Orion. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, March 18, 1925.)

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, March 18, 1925.

DR. WM. C. L. EGLIN, President, *in the Chair.*

Additions to membership since last report, 6.

On motion, duly seconded, the resolution of the Board of Managers recommending the election to Honorary Membership of Professor Pieter Zeeman, of Amsterdam, Holland, and Dr. Elihu Thomson, of Swampscott, Mass., was unanimously adopted.

The Standing Committees of the Institute on Library, Meetings and Museum were announced.

The next business of the meeting was the presentation of the Edward Longstreth Medal, and the Chairman recognized Dr. Geo. A. Hoadley who, on behalf of the Committee on Science and the Arts, introduced Major William E. Hoke, of Washington, D. C., to whom had recently been awarded the Edward Longstreth Medal for his improved method of making and measuring precision gauges. The Chairman then presented the medal and accompanying documents to the recipient who expressed his appreciation of the recognition.

Doctor Hoadley was again recognized and introduced Mr. Daniel H. Meloche, of Detroit, Mich., who was awarded the Edward Longstreth Medal for his method of making long-life molds and their application in the quantity production of castings. The Chairman presented the medal and accompanying documents to Mr. Meloche who thanked the Institute for the honor conferred upon him.

Dr. E. G. Zies, of the Geophysical Laboratory, Carnegie Institution of Washington, was next introduced and presented a communication on "Volcanic Incrustations in the Valley of Ten Thousand Smokes." The speaker gave a brief account of the fumarolic area in the volcanic region of Alaska called the Valley of Ten Thousand Smokes. He described the general characteristics of the incrustations and the probable method by which the various constituents were transported and concentrated. He referred to the mineralogical changes that are liable to take place with the lowering of temperature, and illustrated the subject by a series of colored lantern slides.

After a brief discussion the thanks of the meeting were conveyed to the speaker. Adjourned.

GEORGE A. HOADLEY,
Acting Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, March 4, 1925.)

HALL OF THE INSTITUTE,

PHILADELPHIA, March 4, 1925.

MR. HAROLD CALVERT *in the Chair.*

The following reports were presented for first reading:

No. 2818: Chance Method of Separating Materials of Different Specific Gravities.

No. 2828: Work of Mr. Francis Hodgkinson.

No. 2830: Fynn-Weichsel Motor.

GEORGE A. HOADLEY,
Acting Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, March 11, 1925.)

RESIDENT MEMBERS.

DR. CLIFFORD BANTA, Chief Chemist, Barrett Company, Margaret and Bermuda Streets, Frankford, Philadelphia, Penna.

MR. C. BROWN HYATT, Radio Experimenter, Melrose Park, Penna.

MR. WILLIAM F. JAMES, Manager, Industrial Division, Philadelphia Office, Westinghouse Electric and Manufacturing Company, 30th and Walnut Streets, and for mail—6920 Boyer Street, Mount Airy, Philadelphia, Penna.

MR. R. T. SENTER, Vice-president, Engineering, Mitten Management, Incorporated, 1520 Spruce Street, Philadelphia, Penna.

NON-RESIDENT MEMBERS.

MR. J. KENNETH W. MACALPINE, Chemistry Teacher, Box 39, Hartley Hall, Columbia University, New York City, N. Y.

MR. WM. H. THUROW, Electrical Engineer, 30, Mullerstrasse, Berlin N. 65, Germany.

CHANGES OF ADDRESS.

DR. J. ED. BREWER, S. E. Corner 18th and Cherry Streets, Philadelphia, Penna.

MR. HAROLD CALVERT, Calvert and Barnes, 2114 Sansom Street, Philadelphia, Penna.

MR. H. M. KAUFMANN, 270 Madison Avenue, New York City, N. Y.

MR. A. L. W. WILLIAMS, 59 West 68th Street, New York City, N. Y.

NECROLOGY.

Mr. Chas. A. Hexamer, Bullitt Building, Philadelphia, Penna.

Mr. David H. Lane, 408 Land Title Building, Philadelphia, Penna.

LIBRARY NOTES.

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BOOK REVIEWS.

GRUNDBEGRIFFE DER MECHANISCHEN TECHNOLOGIE DER METALLE. By GEORG Sachs. x–319 pages, 232 illustrations, 8vo. Leipzig, Akademische Verlagsgesellschaft m.b.H., 1925. Price, $3.15.

The author of this work is a co-worker in the Kaiser Wilhelm Institute for investigation of problems in metallurgy and, therefore, has high qualifications for the task. The text of the book shows his merit. It was mainly written to present a comprehensive view of the present state of the extensive information on metallurgy and to consider certain apparent inconsistencies in these data.

Primarily, the work is to set forth the results of research undertaken under strict conditions. Many data heretofore regarded as conflicting are found to be reconciled when thorough investigation is made. Out of the mass of data already accumulated in the extensive and important field of metallurgy, only such materials have been selected as have had practical results. To connect up seemingly discordant and dissociated phenomena has also been a leading object of the author. Phenomena that may seem entirely disconnected may by physical means be correlated, while in other cases phenomena apparently correlated may by physical methods be disconnected. This, indeed, is a feature of all sciences, namely, that they show analogies where ordinary inspection does not indicate them and show differences when close analogy is usually understood. Zoology tells us that a bat is not a bird, and chemistry tells us that glycerol is an alcohol. The content is in the main limited to the fundamentals in the physical and evident phenomena of the broad field of mechanical technology.

A summary of the table of contents will show more exactly the scope of the work. After a brief introduction, a section of nearly one hundred pages on "Tension and Deformation" is given. The second section deals with crystallization and solidification. A third treats of construction and mechanical properties. An interesting and somewhat novel feature of this chapter is a discussion of the relation of periodic classification to the mechanical properties of the metals. Numerous properties of the metals, the author states, are periodic functions of the atomic weights. This statement is illustrated in considerable detail. The recent investigations of the arrangements of atoms in crystals as begun by Laue and continued by other investigators are given consideration, so that the bearings of these apparently somewhat abstruse researches are shown in their practical light.

The work shows an enormous amount of careful collection of data and assiduous sifting of the same so that the vast field may be well presented to the student and practical worker. Many well-executed illustrations add to the serviceability of the book. There are few departments of modern industry requiring more thorough investigation both in the theoretical and practical fields than the great metallurgical procedures, and this book will be of great aid to all who are concerned in these lines.

HENRY LEFFMANN.

CRYSTALS AND THE FINE-STRUCTURE OF MATTER. By Friedrich Rinne. Translated by Walter S. Stiles. Illustrated with plates and over two hundred figures. ix–195 pages, 8vo. New York, E. P. Dutton and Company, no date. Price, $4.20.

The author of this work is professor of mineralogy in the University of Leipzig. The translator does not give himself a local habitat or a title.

In the abundance of works on colloids now issuing, it is a relief to find one giving exclusive attention to the crystalline condition. Colloids are of immense interest and importance, but they are rarely attractive. Even in the field of chemistry they are rather "caviare to the general." Crystals, however, have mostly a charm for all. The development of the method of making thin sections of minerals placed in the hands of the mineralogist and geologist many oppor-

tunities for indentifying individual rock components, and the invention of special modifications of light further extended these possibilities. Of late years, the use of the refractive index has added new lines of identification. In these methods, however, the crystal is considered as a mass, but in the studies presented in the book now in hand, the ultimate atomic arrangements are the object of research. The first German edition of the book was soon exhausted. The present translation is from the second. It has been prepared in collaboration with the author. Considerable new matter was added in preparing the second German edition, all of which has been included in the translation. Among these new materials are historical details, supplemented by portraits of those who have figured most actively in the research in this line. The translation is well done, but few reminiscences of the German idiom being noted. The author includes the fine particles that make up matter, electrons, atoms, ions and molecules, under the term "leptons," from the Greek "leptos," "fine," "delicate." He coins a number of derivatives, terming the study of the subject of the fine-structure of matter "leptology." It is a question whether additions of this kind are necessary or advisable. The progress of science renders the introduction of new terms necessary, and the modern rate of progress brings about the necessity very frequently, but conservative principles should rule in such matters. It seems as if notwithstanding the marked decline in the study of the classical languages in our modern college courses, the two great languages are still near at hand and liable to be frequently drawn on for new words. In another direction, the translator seems in the opinion of the reviewer to have offended slightly. The word "fine-structure," apparently a literal translation from the German, is used extensively. It has a rather German flavor in the compound form, and possibly the translator might have found a more suitable word.

The data given in the book are comprehensive and extensive. The whole subject is one of considerable complexity and of comparatively recent development. A literary flavor is given by information concerning the biography of some of the more important workers in the field, together with portraits. Many illustrations are given, showing arrangements of atoms in crystals. Some attention is given to the structure of amorphous bodies and thus the crystalloid condition (or as Loeb terms it "behavior") is linked up with the colloidal. It seems to the reviewer that the book should contain a somewhat full description of the apparatus employed in this line of work and the methods of applying it. Good diagrams are given of the photographic pictures obtained in the investigations and some reproductions of the pictures themselves, but these would be better understood if the exact method by which they were obtained was described. The data give a most interesting review of what is now known concerning the arrangements of atoms in ordinary molecules, and one wonders what sort of diagram would be required to show the complete structure (including the protons and electrons) in say a crystal of mercuric iodide. There is a good index.

HENRY LEFFMANN.

LES NOTIONS FONDAMENTALES D'ÉLÉMENT CHIMIQUE ET D'ATOME. By George Urbain. 171 pages, illustrated, 12mo. Paris, Gauthier-Villars et Cie., 1925.

This book is one of a series entitled "Science and Civilization," being a concise exposition of human knowledge synthetically considered. The author is well-known in the field of chemistry. It contains an excellent summary of the present state of knowledge and theory on the subjects of definition of an element, nature of radio-activity, constituents of the atom and the structure of the same, properties of the elements in relation to the constitution of the atoms and, lastly, the question of isotopes. The opening chapter gives a valuable and interesting account of the work of Lavoisier and some of his contemporaries. In all parts of the book a cosmopolitan spirit is exhibited, the work of scientists other than French being fully set forth. Much information is given concerning the later developments of radio-activity. Even a superficial perusal of the several chapters gives an almost appalling impression of the complications that have been brought out in the recent physico-chemical researches.

The data are presented carefully and in clear language, but it cannot be denied that many features of these newer views are inherently complicated and that the older chemists, to whom the atom was merely an indivisible, inalterable mass, find the modern views discomforting and difficult. A typographic error, not misleading, however, is noted on page 161, the atomic weight of ordinary lead being given as 107.2 instead of 207.2.

HENRY LEFFMANN.

HELMHOLTZ'S TREATISE ON PHYSIOLOGICAL OPTICS. Translated from the third German edition. Edited by James P. C. Southall, Columbia University. Vol. II, The Sensations of Vision. viii–480 pages, colored plates and illustrations in the text, large 8vo. The Optical Society of America, 1924. Price, $7. This work is not obtainable from booksellers but only through the Optical Society of America. Applications for purchase must be addressed to Prof. F. K. Richtmyer, Cornell University, Ithaca, N. Y.

The volume in hand continues the subject of physiologic optics. The general character of the work was set forth in the review of the first volume. Helmholtz, of course, needs no encomiums from a reviewer. His authority in this field, as indeed in all fields in which he labored, is without superior. The third German edition from which this translation is made was much extended over the preceding issue, with Professors Gullstrand, von Kries and Nagel acting as collaborators. New material in the present issue in English comprises three notes specially prepared by Professor v. Kries and a chapter contributed by Dr. Christine Ladd-Franklin. Kries' contributions are principally on normal and anomalous color sensations and theories of vision. Doctor Ladd-Franklin's chapter is on the nature of color sensations. Her paper on this subject, presented at the International Congress of Psychology in London in 1892, was specifically approved by Helmholtz, who was present.

Great service is rendered to the important field of physiologic optics, indeed, considering the value of the sensation of vision, we may say the most important department of physiology and certainly not the least difficult. As pointed out in Mrs. Franklin's paper, the treatise is on psychology as well as physiology.

The book will afford to all who are interested in light, whether as the

medium of a physiologic function or as a physical phenomenon, ample data for study and investigation. The reviewer feels that he must express regret that the editor has not been willing to spell "color" in the sensible American fashion, but this is perhaps merely a matter of personal feeling. The subjects discussed in the volume in hand are: Stimulation of the organ of vision, Stimulation by light, Changes in the retina due to light (Nagel), Simple colors, Compound colors, Intensity of light sensation, Duration of the sensation of light, Variations of sensitivity, Contrast, Various subjective phenomena. Doctor Nagel contributes an appendix including: Adaptation of the eye for different intensities of light and duplicity theory and twilight vision. A colored plate of the solar spectrum with a duplicate showing how the same appears to the totally color-blind is given as frontispiece. The color plates were made in Germany. The work is in high-class form, the paper, printing and binding being all excellent. The general features of work were set forth in reviewing the first volume. The work will be completed in three volumes at a total cost of twenty-one dollars.

HENRY LEFFMANN.

THEORETICAL AND APPLIED ELECTROCHEMISTRY. By Maurice de Kay Thompson, Massachusetts Institute of Technology. Revised edition, xviii–551 pages, 218 illustrations, 8vo. New York, The Macmillan Company, 1925.

The first edition of this book appeared in 1911 and was written to supply the author's students with a comprehensive summary of applied electrochemistry, as a substitute for note-taking and for the necessity of searching literature. Note-taking is, indeed, as all lecturers know, a very unsatisfactory method of securing information. Students are very liable to misunderstand the words used and are too much given to relying on this method as best adapted to catch the professorial preferences with a view to meeting them in examination questions. Search of literature is time consuming, and as a very large proportion of all scientific literature of importance is in German and a moderate amount in French, difficulties of translation are constantly met. In the study of electrochemistry, experimental work is of great importance and note-taking, as the author observes, is particularly burdensome.

The plan adopted in the first edition was to discuss each subject from the theoretical and technical point of view. In the theoretical part a knowledge of theoretical chemistry was assumed. The same plan has been followed in the present issue, but a special addition has been a treatise on theoretical electrochemistry. All the theory that is of interest or value to the electrochemical engineer has been introduced that could be given without increasing unduly the size of the book. It is worth noting that in the preface to the second edition, the author gives two German works as the principal sources of the text on theory. In the discussion of the ionic theory and the activities of electrolytes a work in English has been used.

The book covers a wide field and the explanations and descriptions are clear and comprehensive. Many illustrations of apparatus exhibit the high development that the electrochemical industries have reached. Considerable

space is given to the subject of nitrogen fixation. Acknowledgment of aid in the preparation of the text is given to many persons and firms. Students of the subject and electrochemical engineers will find the book of great use. A detailed table of contents and an excellent index add to its practical value.

HENRY LEFFMANN.

DIE METHODEN DER THEORETISCHEN PHYSIK. By Felix Auerbach. x–436 pages, 150 diagrams, 8vo. Leipzig, Akademische Verlagsgesellschaft m.b.H., 1925. Price, $3.15.

The author of this work has been engaged for two decades in teaching theoretic physics, in which the chief object after the setting forth of the scope and principles, the subject of a lecture has been demonstration of the methods of the science. These objects have been made the purpose of the work, although, of course, the presentation of the written word has compelled certain modifications from the lecture form. The text is adapted to beginners who have a knowledge of data of experimental physics, and will be also suitable for the teachers who desire to renew the more or less faded recollections of earlier studies, thus to fit themselves for better methods of instruction.

Beginning with fundamental conceptions and principles, systematic development of methods is carried out; textual explanations are supplemented by mathematical elucidations and the exposition proceeds, from the elementary to the advanced, from the infinitesimal to the statistical, from arithmetic to geometric methods. Long experience and many expressions from others have convinced the author of the need for the work in a wide circle. In fact, only one complete work of similar scope is available—Riemann-Weber's "Partiallen Differentialgleichungen." The first volume of Courant and Hilbert's "Methoden der Mathematischen Physik" has just appeared. Both these books have been prepared by mathematicians, while the work in hand is by a physicist. Comparison of the other two books with his own, the author assures us, shows that they have but little in common, particularly that by Courant and Hilbert, which is specially adapted to highly advanced workers, and devoted almost exclusively to data of most recent origin. The present book contains information concerning the general technique of many years past, methods that have brought theoretical physics to its high position of to-day.

Notwithstanding the limitation of the book to a materialistic science, the author finds opportunity to discuss a philosophic point. In the chapter on "Wortsprachliche Methodik," he enters upon the question whether thought without speech is possible. One extreme is that no thought is possible without expression in words, the other that expression dilutes, distorts and may even suppress thought. He refuses, however, and very wisely, to make an argument on this line, but notes, as all scientists are aware, that the ordinary resources of a language do not suffice for the terms of a science. The points raised by these considerations are taken up at some length but need not be further considered here.

The work is comprehensive and thorough, the make-up is excellent, the numerous diagrams add greatly to the clearness of the text, and it presents itself as a valuable and useful contribution to the literature of physics.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 195, Standardization Tests of N.A.C.A. No. 1 Wind-tunnel. By Elliott G. Reid. 31 pages, illustrations, quarto. Washington, Government Printing Office. Price, ten cents.

The tests described in this report were made in the 5-foot atmospheric wind-tunnel of the National Advisory Committee for Aeronautics, at Langley Field, with the primary object of collecting data on the characteristics of this tunnel for comparison with those of others throughout the world, in order that, in the future, the results of tests made in all the principal laboratories may be interpreted, compared, and coördinated on a basis of scientifically established relationships, a process hitherto impossible due to the lack of comparable data.

The work includes tests of a disc, spheres, cylinders, and airfoils, explorations of the test section for static pressure and velocity distribution, and determination of the variations of air-flow direction throughout the operating range of the tunnel.

Report No. 199, Interference Tests on an N.A.C.A. Pitot Tube. By Elliott G. Reid. Eight pages, illustrations, quarto. Washington, Government Printing Office, 1925.

In connection with the standardization of instruments used in the wind-tunnel, this investigation was undertaken at Langley Memorial Aeronautical Laboratory, to determine the nature and magnitude of the errors inherent in the measurement of air-speed by a Pitot tube when the instrument is mounted close to some other body. The mounting of the instrument in proximity to some other body is so frequent in flight and in wind-tunnel research that it seemed advisable to investigate thoroughly the magnitude of the possible errors caused by such proximity. The results of this investigation will facilitate comparisons of the errors due to interference which have been reduced to percentages of the air-speed readings obtained under conditions of no interference.

Report No. 202, Sparking Voltage of Spark Plugs. By Francis B. Silsbee. 16 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, five cents.

This report has been prepared in order to collect and correlate into convenient and useful form the available data on this subject. The importance of the subject lies in the fact that it forms the common meeting ground for studies of the performance of spark generators and spark plugs on the one hand and of the internal-combustion engines on the other hand. While much of the data presented was obtained from various earlier publications, numerous places were found where necessary data were lacking, and these have been provided by experiments in gasoline engines at the Bureau of Standards.

The principal variables which affect the sparking voltage are the length of the spark gap, shape of the electrodes, gas density, electrode temperature, mixture ratio and turbulence. The report also contains a brief description of the time lag effects in spark gaps, which is particularly important in the case of the standard gaps used in testing ignition apparatus.

Report No. 203, Accelerations in Flight. By J. H. Doolittle. 18 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, ten cents.

This paper, published by the Committee, was presented to the Massachusetts

Institute of Technology in partial fulfilment of the requirement for the degree of master of science.

This work on accelerometry was done at McCook Field for the purpose of continuing the work done by other investigators and obtaining the accelerations which occur when a modern high-speed pursuit airplane is subjected to the more common manœuvres.

The accelerations obtained in suddenly pulling out of a dive with well-balanced elevators are shown to be within 3 or 4 per cent. of the theoretically possible accelerations.

The maximum acceleration which a pilot can withstand depends upon the length of time the acceleration is continued. It is shown that he experiences no difficulty under the instantaneous accelerations as high as 7.8 g., but when under accelerations in excess of 4.5 g., continued for several seconds, he quickly loses his faculties.

PUBLICATIONS RECEIVED.

Introduction to Theoretical Physics. Vol. I. By Arthur Haas, Ph.D., translated from the third and fourth editions by T. Verschoyle, M.C., with a foreword by Prof. F. G. Donnan, F.R.S. 331 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1925. Price, $6.

Lecture and Laboratory Experiments in Physical Chemistry, by Henry S. Van Klooster, Ph.D. Second edition, revised and enlarged. 274 pages, illustrations, 12mo. Easton, Penna., The Chemical Publishing Company, 1925.

Le Livre du Cinquantenaire de la Société Française de Physique. 160 pages, illustrations, plates, 8vo. Paris, Revue d'Optique, 1925. Price, in paper, 17 francs.

Callinicus: A Defence of Chemical Warfare, by J. B. S. Haldane. 84 pages, 16mo. New York, E. P. Dutton and Company, 1925. Price, $1.

Ontario Department of Mines. Thirty-first Annual Report, being vol. 31, part I, 1922. 73 pages, plate, 8vo. Toronto, King's Printer, 1924.

National Advisory Committee for Aeronautics. Technical Notes, No. 214. Note on the Katzmayr Effect on Airfoil Drag, by Shatswell Ober. 11 pages, plate, quarto. No. 215, The Calculation of Wing-float Displacement in Single-float Seaplanes, by Edward P. Warner. 5 pages, illustrations, quarto. Washington, Committee, 1925.

CURRENT TOPICS.

Why Wireless Electric Rays Can Bend Round the Earth. Sir Joseph Larmor. (*Phil. Mag.*, Dec., 1924.)—"The earliest announcement that electric signals through free æther had been successfully detected as far as America by the Marconi operators, gave rise to a prompt query from the late Lord Rayleigh as to how the rays could manage to bend round the protuberance of the curved earth. . . . But nowadays, when ray-signals are readily received at the antipodes, all shadow of uncertainty as to the facts is removed. The rays could not travel free, except in straight lines, in a medium of practically uniform speed of propagation such as ordinary air; either they must be guided by being linked to the surface of the earth, much as cylindrical Hertzian waves follow a guiding central wire, or else the speed of propagation must for some cause increase notably upward so as to bend them down." The question is, if we accept the latter alternative, how shall the greater speed in higher regions be accounted for. One possibility that has been suggested is the ionization of the upper regions of the atmosphere by the action of ultra-violet radiation from the sun. Such ionization, to be adequate for the increase in velocity of the waves, would, unfortunately, at the same time damp them out. "To produce sensible bending of the rays without extinction, all action by conductive or other dissipation must thus be excluded. . . . A theory satisfying this criterion was hammered out in class lectures at Cambridge on electric waves last February, and has been, in fact, already expounded in answers in the Mathematical Tripos."

"A sufficient cause for the increase of velocity, without dissipation, for waves travelling horizontally is, in fact, afforded by the free oscillation of ions even sparsely distributed in the very high regions of the atmosphere; though lower down their energy would be dissipated by collisions with the atoms and the travelling waves would be gradually quenched. Current is transmitted without any frictional loss across the vacuum of an electric valve by the jet of free electrons. On the other hand, in conduction in a metal the electrons or light ions get up speed at very rapid rate under the electric field, but at the end of each short free path they render up by collision part of the energy so acquired to the obstructing atoms of the metal, and this dissipation of the energy of the field is the measure of the electric resistance. . . . For ions travelling in an intensely rarefied upper atmosphere the free path will be long, so that many alternations of the electric force of the field of radiation, even for long electric waves traversing the medium, may occur within the time of one ionic path. This involves that the travelling ions will in the main swing free under the influence of the waves and thus interact without the dissipation of their energy, scattering by secondary radiation

from the slowly oscillating ions being negligible: There will thus be an influence on the velocity of the waves without absorption. To suit the present explanation, the change ought to be a substantial increase, notwithstanding the small number of the ions contributing to it in the ultra-rarefied upper atmosphere. And the reason is simple. The influence of an ion is measured (joined with the time) by the mean value of the alternating value of the alternating velocity excited in it and this for a given intensity of field is proportional to the period of the waves, so that for long electric waves the effect may be millions of times as great as for short waves of comparable energy—in fact, it involves the square of the wave-length.

"There must thus be a layer high almost beyond the sensible atmosphere, within the auroral domain, in which a sheaf of horizontal electric waves, provided they are long enough, will travel without loss by absorption or scattering, concentration in this stratum being due to the potent influence exerted on the velocity of long waves by the free ions of small inertia interacting with them. But we have to suppose that the energy transmitted in this high stratum is being shed down to a sensible degree all along the path, for the signals to be everywhere received. Introducing optical imagery, we can contemplate a special component ray-sheath connecting the transmitter to every receiver situated along the path of the beam; these rays all gather together into a sort of caustic curve or layer up aloft, and so long as they are in it the energy travels onward without loss except by sideway spreading."

The author then proceeds to elaborate the quantitative side of his theory. At auroral heights the mean free path of the atoms is calculated to be several centimetres and the number of molecules per cubic centimetre is about 10^{15}. A formula is derived giving the relation between the increased velocity of wave-transmission and the normal velocity. "For long electric waves it would be sensible, notwithstanding extreme tenuity of the gaseous ions. It would usually be of no account except in metals for the short waves of light."

To get for the rays a curvature equal to that of the earth, there will need to come into play in the highest regions only about 500 hydrogen ions per cubic centimetre out of the 10^{15} molecules present in the same volume of gas. A study of the amplitudes and times of oscillation of the ions shows that they fit in with the theory advanced, and for energy relations it is computed that for a wave-length of 1 km. the effect of ionic absorption over a stretch of 10,000 km. reduces the flow to 1/2.7 of its initial value. The conclusion is given: "We infer that the present type of explanation by a velocity of propagation increasing with height, which bends down the rays without undue absorption, is sound and reasonable for electric waves of the lengths usually employed, if only a very small proportion of the molecules of the upper air were ionized so as to provide electrons or light ions, by the intense ultra-violet solar radiation."

To anyone who has heard Sir Joseph Larmor, at a meeting of the British Association for the Advancement of Science, discuss subject after subject and always clarify and illuminate whatever theme he touches upon, it will not be a matter of surprise that he has rendered the same fine service to the vexed question in the title of this paper.

G. F. S.

Controlled Orbital Transfers of Electrons in Optically Excited Mercury Atoms. R. W. WOOD. (*Proc. Roy. Soc.*, A 740.)—"As I have shown in numerous publications, the vapor of mercury *in vacuo*, even at temperatures below the solidifying point of the metal, when illuminated by the light of a water-cooled quartz-mercury lamp, emits the monochromatic radiation of wave-length 2536. According to Bohr's theory, this resonance radiation results from the fall of an electron from the $2p_2$ orbit, to which it has been raised from the $1S$ orbit by the absorption of one quantum of 2536 radiation, back to the $1S$ orbit, the orbit occupied by the electron when the atom is in its normal state." When the electron is on the $2p_2$ orbit, it may go farther from the nucleus of the atom at the centre and move about the nucleus in one of the several orbits that lie outside of $2p_2$. To which one of them it arrives will depend upon the amount of energy that it absorbs, for it must have energy expended upon it in order to go farther from the positive charge of the nucleus which is attracting it. The more energy imparted to it the farther out it can go. When it returns to some orbit nearer to the nucleus it may go first to some orbit that it passed over in moving outward. Radiation is emitted as it comes inward, and the farther it moves toward the centre at one step the shorter is the wave-length of the radiation sent out as a result of that change of position.

Professor Wood gets some strange experimental results. He has two sources of radiation with which to illuminate a tube containing mercury vapor, one a water-cooled mercury arc, the light from which passes through a filter of bromine vapor, the second, another quartz arc not water-cooled. Let the first shine upon the mercury vapor. No visible light results, though two ultra-violet lines are there. After the extinction of the source just used, let the second be tried. It also fails to make the mercury vapor luminous. When the two sources act together on the vapor it emits a green line and two others in the violet. What has taken place is this. The light through the bromine filter contains the line above mentioned, 2536, and this has raised an electron from $1S$ to the $2p_2$ orbit. Then the electron in this condition has absorbed energy from the violet line furnished by the unshielded arc and has gone out to the $2s$ orbit; from this it has fallen inward to orbits $2p_1$, $2p_2$ and $2p_3$, emitting the green line 5461 and 4358 and 4046, respectively. A single electron cannot act thus, but a part of the electrons go to one orbit, a second part to another orbit, and so on.

It is possible to explain even the intensities of the resonance line obtained on the basis of Bohr's theory.

G. F. S.

The Magnetic Moments of Atoms. W. GERLACH and A. C. CILLIERS. (*Zeit. f. Physik*, Vol. 26, No. 2, 1924.) **Quantizing of Direction in the Magnetic Field.** W. GERLACH and O. STERN. (*Ann. d. Physik*, Vol. 74, No. 16, 1924.)—A preliminary report on this subject will be found on page 114 of this JOURNAL for July, 1924. In the quantum theory of magnetism and of the Zeeman effect, the assumption is made that a certain vector related to the atom can hold in a magnetic field only certain definite and separate angles with respect to the direction of the magnetic force. A deduction from this is that in hydrogen gas traversed by a magnetic field, the planes of all the electrons in the different atoms are at right angles to the magnetic force. If now a ray of light passes through the gas in a direction perpendicular to the magnetic force and, consequently, parallel to the planes of the electrons, the component of the electric vector that is parallel to the magnetic force strives to displace the electrons from their orbital planes, while the component at right angles to the same force tends to displace them in their planes. The gas should, therefore, show double refraction which ought to be independent in its amount of the strength of the magnetic field. The same result would be expected in other elements also, but at least up to the summer of 1921 no such effect had been observed.

In a paper published in 1921, Otto Stern sketched an experiment that would decide whether the classical or the quantum theory furnishes the correct prediction in the field of phenomena just discussed. He suggested the sending of a tiny jet of atoms parallel to the sharp edge of a magnetized wedge, and their reception on a plate at the end of their course. Without the magnetic field the jet would form a circular spot on the plate. With the presence of the field the quantum theory predicted that the circular spot would transform itself into two spots in which the distribution of intensities depends on the quantum relations of the atoms concerned. At the position of the original spot there should be a minimum of intensity. Just here the classical theory requires that, under similar conditions, a maximum of intensity should manifest itself. The issue between the two theories was thus very sharply drawn. When the experiment was tried in a vacuum with silver, no deposit at all could be detected in the middle of the spot. Hence it was the quantum theory that was endorsed by experiment.

Be it noted, however, that a decision founded upon experiments made with a single element could scarcely be regarded as final. It is, therefore, well that the experiments have been continued with a wider range. Improvements were made in the method of aligning the hole in the furnace, the first screen, second screen, edge of wedge and receiving plate. This afforded much difficulty in the first experiment. In many cases of the later series the spot received on a glass plate was developed with silver nitrate solution. In others the jet of atoms continued until the deposit was visible without development. At a distance of .15 mm. from the wedge-shaped edge of the electro-

magnet the strength of the magnetic field was 17,500 gausses and its rate of variation along a line perpendicular to the edge was 23,600 units per cm. At a distance of .6 mm. from the same edge the two corresponding quantities were 12,800 and 7600 per cm. With silver the original circular spot was .13 mm. in diameter. This by the action of the magnetic field was distorted into a rough ellipse .13 mm. as before in a direction perpendicular to the magnetic field, but .20 mm. along a line at right angles to the edge and to the atomic ray. Speaking of silver, Gerlach and Stern say, "The spots obtained are in entire agreement with those predicted by the quantum theory. No trace was discovered of atoms that were not deflected in the magnetic field."

It is in the work of Gerlach and Cilliers that we find the extension of the experiments to other elements than silver. They used apparatus in which the atomic jet had either a total path of 9 cm., of which 3 cm. was in the magnetic field or a total path of 15 cm., 4.5 cm. of which was in the field. They continued the experiment with silver so long that the deposit was visible without the use of a developer, yet there was no evidence of the presence of atoms that came through the field without deflection. "All normal silver atoms receive direction in the magnetic field."

Copper was evaporated at 1500° or 1600° abs. The effects obtained were just like those with silver except that they were smaller in the separation attained. "The copper atom in the normal state has a magnetic moment of one Bohr magneton." In order to study the side of the hollow spot on the glass plate caused by those atoms that were attracted toward the magnetized edge in comparison with the opposite side due to the repelled atoms, an experiment was performed in which the atoms nowhere traversed a field that had any considerable change of strength from one margin of the jet to the opposite one. Sufficient copper was evaporated to give a deposit visible without development. "No difference of intensity between the attracted and the repelled spots could be seen. They were entirely symmetrical and of equal width. By the magnetic field as many atoms are sent in one direction as in the other. The field strength was about 12,000 gausses and the rate of change with distance from the edge about 100,000 gausses per cm."

In the cases of silver, copper and gold, the separation of the jet under the influence of the magnetic field is in line with deductions drawn from the quantum theory, and these three atoms possess magnetic moments equal to one Bohr atom apiece.

Tin gave inconclusive results. No separation of the atomic jet into two parts was definitely recognized, though there was some reason for believing that magnetic atoms were present in the jet. Thallium, lead and bismuth were received on plates cooled by liquid air. The thallium spot was broadened by the magnetic field, but there was no distinct separation into two parts sundered by a portion

of the glass plate on which no atoms at all had impinged. The atom of this element seems to have a magnetic moment equal to one-third of a Bohr magneton.

Lead gave most interesting results. "No effect of the magnetic field was found. The deposit left by the atomic jet is as sharply bounded when the magnetic field acts as in its absence. The atom of lead in the normal state is not magnetic." Bismuth, on the contrary, displayed a marked effect of the magnetic field. "The atomic jet was separated into two clearly limited parts, one of which was due to attraction toward the edge, while the other owed its origin to atoms that came through the magnetic field without deflection. The displacement of the attracted ray amounted to .65 mm. A control experiment with silver that was intercalated between two experiments with bismuth showed that the lack of symmetry did not have its origin in the apparatus." The promise given by the authors that this series of experiments is to be continued is welcome for, in the opinion of the reviewer, no more important work than this has been done in the physical laboratories of Germany for a long time.

G. F. S.

The Fundamental Problem in the Field of Atmospheric Electricity. H. BENNDORF. (*Physik. Zeit.*, Jan. 1, 1925.)—Thanks to the investigations conducted by L. A. Bauer for the Carnegie Institution, it is now known that over all the earth for the greater part of the time a current of electricity flows downward from the air to the earth. The average current strength is .000002 ampere per sq. km., or 1000 amperes for the entire earth. Balloon observations show that the quantity of this vertical current per unit area remains the same up to an elevation of 9 km.

The electrical condition of the earth is roughly this. It has a charge of 800,000 elementary quantities of electricity per sq. cm. At a height of 60 km. the sphere of the earth is surrounded by the sphere of the stratosphere, which is conducting. The intervening air is slightly conducting and its conductivity increases from the earth upward. Twelve hundred elementary units reach the earth per second on each sq. cm. Six hundred positive units each second leave the stratosphere per sq. cm. and go downward and the same number of negative units reaches the same surface in the same time. "The fundamental problem of the electrical economy of the earth is, 'What processes maintain this continuous current and what are the sources of its energy?' Since it can be easily shown that, upon the removal of the cause of this current, the negative charge of the earth would quickly disappear, the problem is often phrased thus, 'What agency keeps up the negative charge of the earth?'" To make progress toward an answer the author tabulates all possible origins of the current and proceeds to examine them critically. He rejects as incompetent to account for the result the action of the electric field, gravitation, the pressure of radiation and convection. There remains

only to regard the vertical current as due to the inertia of particles, whether these come to the earth from the sun, or are produced in the air by radio-active disintegration, or are hard β-rays developed in the air by high-altitude radiation. All these possibilities are alike in depending upon β-rays in some way. Hence all are opposed by the failure of both Schweidler and Swann to detect such rays by experiment. The author, however, is not convinced that the fruitless experiments are absolutely decisive. A second objection is this—the β-rays requisite to account for the current would bring about 20,000 times as much ionization of the air as actually exists. Swann, however, made it appear probable that β-rays travelling with a velocity almost that of light fail to produce ionization of the air.

From the domain of terrestrial magnetism further perplexity is joined to the matter of vertical currents. L. A. Bauer has considered the earth to be divided into two polar caps and an equatorial zone by the two parallels of latitude, 45° N. and 45° S. He has calculated the line integral of the horizontal magnetic force around each of these parallels. From the values of these integrals it seems certain that there are vertical currents of large magnitude. In both polar caps negative electricity comes to the earth. In the northern hemisphere the total current is 1,940,000 amperes, and in the southern it is 1,600,000 amperes. In the equatorial zone negative electricity streams upward from the earth, the total current being 3,540,000 amperes. Compared with these high-current values the 1000 amperes of vertical current spoken of earlier is a mere bagatelle. Certain considerations go to show that these enormous currents must be explained by β-rays, as was also true in the case of the 1000 amperes. "It is at any rate sure that, when we once get an explanation for the system of Bauer's vertical currents, we shall have at the same time the solution of the fundamental problem of atmospheric electricity."

The author offers the following theory of the phenomena before us. The sun sends to the earth β-rays of high velocity of which a part are absorbed in the upper region of the atmosphere and may have to do with the production of the aurora. They give rise to hard γ-radiation and get through the air to the polar caps at least. "To explain the currents of Bauer we assume that, according to the nature of the surface of the earth and to the direction and strength of the γ-radiation, β-rays of high velocity either impinge upon the earth or leave it. In the polar caps the former predominates and in the equatorial zone the latter. In consequence of the change of the direction of the vertical current with locality there will be currents in the earth between the polar and the tropical regions." There is no claim made that this is either a full or an entirely defensible explanation. G. F. S.

A Lecture Experiment in Resonance. R. WACHSMUTH and W. SCHUETZ. (*Physik. Zeit.*, Jan. 1, 1925.)—The common method of demonstrating resonance is by causing a tuning-fork to vibrate

and by letting the sound waves it thus emits fall upon a second fork of the same pitch, which is thereby set in vibration. Leonardo da Vinci was acquainted with an equivalent experiment as he states in his journal. He tells how the string of a lute is made to vibrate by the sounding of a string of the same pitch on another instrument. "And this wilt thou see by applying a bit of straw to the string."

A very modern rendering of the experiment is this. Near to one prong of the receiving tuning-fork is mounted a telephone receiver from which the diaphragm has been removed. As soon as the fork begins to vibrate in unison with the emitting fork, the prong by its approaching to and receding from the coil in the receiver generates therein a weak alternating current. This sent through an amplifier gives rise to a direct current sufficiently large to be used for measurements. A fork of 461 vibrations per second was employed, mounted on its resonance box. A labial pipe of variable pitch served as the source of sound waves. When the frequencies of the pipe were 500, 474, 461 and 449, the corresponding deflections of the galvanometer, caused by the direct current, were about 10, 130, 495 and 55. The deflections of the galvanometer can be thrown on a screen and thus in this demonstration the eye may replace the ear.

G. F. S.

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